

Mats Bohgard

**PARTICLE INDUCED X-RAY EMISSION ANALYSIS
AND COMPLEMENTARY TECHNIQUES FOR EXAMINATION
OF AEROSOLS IN THE ENVIRONMENT
OF INDUSTRIAL WORKERS**



Lund 1983

PARTICLE INDUCED X-RAY EMISSION ANALYSIS AND COMPLEMENTARY
TECHNIQUES FOR EXAMINATION OF AEROSOLS IN THE ENVIRONMENT
OF INDUSTRIAL WORKERS

av

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Errata

<u>page</u>	<u>line</u>	<u>change</u>	<u>to</u>
XII	3 ⁻	$\mu\text{g}/\text{cm}$	$\mu\text{g}/\text{cm}^2$
XIII	10 ⁺	8-9	7-8
3 (caption, figure 1)	1 ⁻	180	180 ⁰
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Abstract Methods, based on PIXE (Particle Induced X-ray Emission Analysis) and complementary techniques, for the examination of aerosols in working environments have been applied and further developed. The potential of Particle Elastic Scattering Analysis (PESA) as a complement to PIXE is discussed and a calibration technique for PESA is described. PIXE detection limits for common aerosol collection substrates have been determined with 2-5 MeV protons and 7-8 MeV He ions as projectile particles. A procedure for determining chromium in aerosol samples including PIXE, ESCA (Electron Spectroscopy for Chemical Analysis), TEM (Transmission Electron Microscopy) and spectrophotometry with DPC-reagent (sym-diphenylcarbazine) has been developed. The procedure was applied to aerosols from thermal spraying operations. Hexavalent chromium was detected in the fine particle fractions. A personal aerosol sampler giving time- and size-fractioned samples for PIXE analysis has been developed. Sampling times of 15 minutes and irradiation times of 10 s are sufficient for determining most elements of hygienic interest in concentrations far below their hygienic threshold limit values. The performance of the sampler was tested for internal losses and separation characteristics between the size fractions.			
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EXAMINATION OF AEROSOLS IN THE ENVIRONMENT OF INDUSTRIAL WORKERS

by

MATS BOHGARD

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SUMMARY

Introduction

Particulate air pollution in working environments is an old problem. Long before analytical and sampling techniques were used for studying the air quality, certain diseases were connected to specific occupations. A great number of workers suffered from damages to their health caused by air pollution in their working environments before the source of the cause of the damage became known. These victims provided the only source of information about the hazards. The increased usage of instruments for detailed studies of aerosols (airborne particles) has, in several cases, made it possible to determine the critical features of the aerosols in terms of health hazards. Industrialization and the accelerated development of new processes, new techniques and new materials have introduced new potential hazards. This development puts high demands on instruments and methods to obtain fast reliable information on new threats to our health.

My aims and efforts have been to develop measuring procedures and instruments for studying and evaluating the effects of the working environment on human health. It should however be remembered, that though instruments and methods from a number of disciplines have been used, the subject of the present thesis is only a very small fragment of our total working environment and that increased knowledge in this area, does not automatically lead to improvements in the environment. The fact is that numerous workers have continued to suffer from diseases caused by unhealthy environments long after the relations between exposure and health effects were known.

The present work is on the application and development of methods which make it easier to identify health hazards in the air of working environments, and will hopefully lead to an increased knowledge about how health hazards are connected to exposure to various airborne particles. The work is based on the sensitive analytical method, PIXE (Particle Induced X-ray Emission analysis), which was introduced at the Department of Nuclear Physics in Lund in 1970 (1).

Aerosol characterization in working environments

By making measurements on aerosols in working environments it will be possible to evaluate the hazard potential in cases where the relations between exposure and effects are known. However, these relations are often not known and then aerosol characterization can be used, together with epidemiological and toxicological studies, to find such relations. By studying aerosols the understanding of the mechanism of aerosol formation can be increased, giving opportunities to develop safer working processes. An increased knowledge of aerosol properties may also be useful when improving elimination techniques and for the development of monitoring routines.

The air pollution situation in working environments is often very complex. Many chemical agents may be present with rapid and large variations in concentration and character, requiring efficient sampling techniques and analytical methods. The most interesting properties, in terms of health effect assessments, are particle concentration, particle size distribution, chemical composition and morphology of the particles.

PIXE and complementary methods

In PIXE analysis samples are bombarded with protons or helium ions from an accelerator. Through this bombardment vacancies are created in the inner shell of the atoms of the sample. On de-excitation characteristic X-rays are emitted. The X-rays are detected with an energy-dispersive detector and an energy spectrum is recorded. By measuring the energies of the X-rays, the elements in the samples can be determined. By measuring the intensity of the X-rays it is possible to quantify these elements.

PIXE has several features which are ideal for small aerosol samples:

1. PIXE is multielemental. In aerosol samples it is normally possible to simultaneously quantify elements with atomic number greater than 14 (above silicon) with high accuracy and precision.

2. PIXE has high sensitivity and low detection limits. It is possible to detect as little as 10^{-9} - 10^{-12} g of the elements.

3. The method is fast. Irradiation times from 10 s to a few minutes are often sufficient for the analysis of working environment aerosol samples.

4. Small samples can be analysed which means that small samplers can be used for aerosol collection and that sampling with moderately sized equipment gives a sufficient quantity of the specimen for the application of complementary chemical analysis.

5. During particle bombardment in the PIXE analysis it is possible to detect signals caused by interactions between the particles and the nuclei of the light elements which cannot be analysed with X-ray methods.

Simultaneously with the detection of X-rays in PIXE-analysis, it is possible to detect particles elastically scattered from the nuclei of the sample atoms. Detection of elastically scattered particles gives information on the light elements which cannot be analysed with PIXE. The energies of the scattered particles yield information on the masses of the target nuclei. The intensity of the scattered particles is a measure of the abundancies of the different nuclei present. The projectile energies normally used in PIXE are not sufficiently high to resolve all the light elements which cannot be analysed with PIXE in aerosol samples. Figure 1 shows an energy spectrum from a sample of small particles from aluminium welding and figure 2 shows a spectrum from an aerosol sample from shielded metal arc welding. The samples were irradiated with 6.2 MeV protons and 12.8 MeV He ions respectively. These energies are somewhat high for the lowest possible detection limits in PIXE analysis. At lower energies, elastic scattering analysis may, however, be used in special applications for single elements or when only a few elements are abundant in, for example, thin aerosol samples. A discussion of the potential of elastic scattering analysis is given in paper I and a calibration

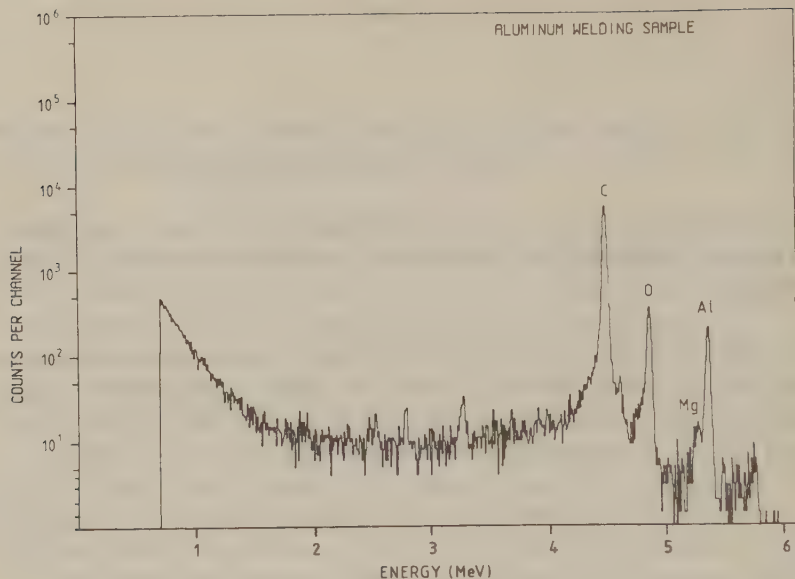


Figure 1. Spectrum of 6.2 MeV protons elastically scattered at 155° scattering angle. A sample of particles from aluminium welding was irradiated by $13 \mu\text{C}$ protons. The sample contained $2.9 \mu\text{g}$ aluminium and $0.9 \mu\text{g}$ oxygen. The carbon peak originates from a polystyrene backing.

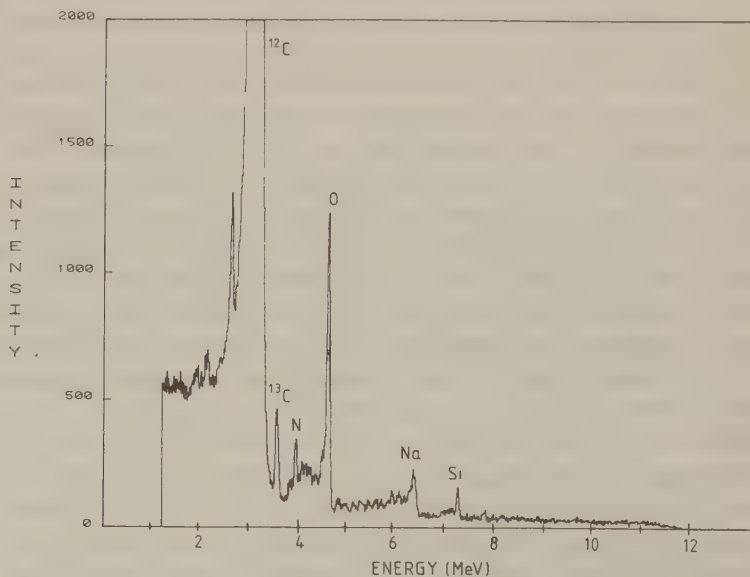


Figure 2. Energy spectrum of 12.8 MeV He ions ($23 \mu\text{C}$) scattered from a welding fume sample. The light elements oxygen (20 ng), sodium (50 ng) and silicon (25 ng) are components of the aerosol sample.

procedure is described in paper II.

In order to find parameters for a suitable combination of PIXE with complementary nuclear methods, PIXE detection limits with protons and He-ions from a 3 MV accelerator were determined (paper III). The results show that projectiles with energies of 2-5 MeV for protons and 7-8 MeV for He-ions give sufficient sensitivities for many aerosol applications. This makes it possible to choose energies to suit complementary techniques for simultaneous analysis.

Knowledge of the elemental composition of an aerosol is often not sufficient for health effect assessments. For aerosols containing chromium, the oxidation state of the metal and the solubility of the chromium compound is of importance. In paper IV an analytical procedure for obtaining detailed information on chromium in an aerosol is described. The procedure includes the analytical methods PIXE, ESCA (Electron Spectroscopy for Chemical Analysis), spectrophotometry with DPC-reagent (sym-diphenylcarbazide) and TEM (Transmission Electron Microscopy). The procedure and sampling techniques designed to suit the analytical methods were applied to a study of aerosols emitted from thermal spraying processes (paper V).

The features of PIXE for fast analysis of small samples have made it worth-while to develop a small personal sampler, dividing the particles into two fractions according to size, for time-resolved sampling. The sampler is described in paper VI and its performance for various particle sizes is described in paper VII.

Dissertation

The present work started in 1976 and is part of the development of PIXE and its applications which has been continuously going on at the Department of Nuclear Physics in Lund since the introduction of the method in 1970 (1). This work is to a great extent based on the PIXE facility in Lund described by K.G. Malmqvist et al. (2) and of which the calibration and stability have been described by G.I. Johansson et al. (3).

Paper I

The lightest elements cannot be analysed with PIXE due to the low energies of their characteristic X-rays. In contrast to other X-ray methods it is possible to obtain quantitative information on these elements simultaneously with X-ray detection. Detection of particles elastically scattered from nuclei of the atoms of the light elements is an attractive complement to PIXE. Protons and He ions with energies obtainable from a 3 MV tandem accelerator may be used for sufficiently thin samples of fine particles. The elemental resolution is limited by the sample thickness. Calculations show that it is possible to resolve interesting elements with atomic mass number below 20 when high particle energies are used (5-6 MeV protons and 8-9 MeV He ions). Lower energies may be used for special applications. Analytical sensitivities for 2.5 MeV and 5 MeV protons vary between 1 and 100 scattered particles/ $(\mu\text{C}\cdot\text{msr}\cdot\mu\text{g}/\text{cm}^2)$

Paper II

Simultaneous detection of X-rays and elastically scattered particles facilitates the calibration procedure in particle elastic scattering analysis. A procedure using polystyrene foils spiked with cobalt to known concentrations is used to study how the number of particles elastically scattered by carbon nuclei depends on the foil thickness. For foil thicknesses greater than 200 $\mu\text{g}/\text{cm}^2$, significant deviations from linearity were found to occur. The deviation seems to be due to detection of doubly-scattered particles in the matrix. Particle

elastic scattering for carbon analysis may be performed for samples deposited on a silver aerosol filter, a gold foil or the spiked polystyrene foil. In the latter case the cobalt determination facilitates the subtraction of background carbon signals, emanating from the polystyrene foil.

Paper III

In order to find optimal parameters for a combination of PIXE with complementary accelerator based techniques PIXE detection limits, regarding K X-rays, of some common aerosol substrates, were determined for 2-5 MeV protons and 8-9 MeV He ions.

Protons of 2 MeV and He ions of 8 MeV have equal velocity. According to simple theoretical calculations regarding characteristic and background X-ray production, detection limits using He-ions should be 2-4 times lower than when using protons when samples are bombarded with projectiles of equal velocity and number. The experiments showed that the detection limits obtained with He ions were less favourable than these predictions, due to higher background in the spectra for medium and high X-ray energy. This may be caused by γ -radiation being Compton-scattered in the detector. In addition, the higher energy transfer from projectile to substrate for He ions puts higher restrictions on maximum beam intensity to avoid damage to the substrate.

The choice of particle and energy for minimal detection limits has to be a compromise between optimum analysis for low-Z and high-Z elements. However, detection limits using 2-5 MeV protons and 7-8 MeV He ions are sufficiently low for many aerosol applications and the choice may be made for optimal conditions for complementary nuclear methods for the simultaneous detection of light elements.

Paper IV

For aerosols containing chromium knowledge about the elemental composition is not sufficient for health effect assessments. The

oxidation state of chromium and the solubility of the chromium compound is of importance. An analytical procedure using PIXE, ESCA, TEM and spectrophotometry with sym-diphenylcarbazide gives detailed information about chromium in the particles. PIXE measures the total chromium content and other elements which may impede analysis with the complementary methods and which may be constituents of the chromium compound. ESCA measures the oxidation states of chromium on the surface of the particles. Using TEM the structure of the particles is determined to obtain information on the homogeneity of the particles. Spectrophotometry with DPC-reagent was used for determining the soluble part of Cr(VI). The procedure was applied to aerosols emitted from shielded metal arc welding on stainless steel. Both Cr(VI) (the oxidation state of chromium posing the greatest health hazard) and Cr(III) were detected in the fumes. When performing ESCA analysis care has to be taken since the reduction of Cr(VI) to Cr(III), caused by the X-ray irradiation in ESCA, has been observed.

Paper V

Thermal spraying is a technique which is of increasing importance in the engineering industry. The technique is used for coating objects with protective surface layers. A material is heated and brought to the object by a gas jet. Applications of the technique can give rise to high aerosol emission. The analytical procedure described in paper IV, in combination with sampling techniques suiting the procedure, was applied for the characterization of the aerosols produced by spraying materials containing chromium and nickel with various spraying methods. A large part of the aerosol mass was found in the respirable fraction (aerodynamic diameters below 5 μm) and hexavalent chromium was detected in this fraction. The mass median aerodynamic particle diameters were below 0.5 μm for particles in the respirable fraction.

Paper VI

A personal low-weight aerosol sampler was developed giving time- and size-fractioned sampling. Coarse particles are collected by impaction and fine particles by filtration. The collection efficiency of the

filter was measured by using monodisperse submicron particles.

PIXE analysis with short irradiation times (10 s) gives detection limits sufficiently low for the determination of most elements of interest far below their hygienic threshold limit values.

A simple test of performance which was carried out in a welding workshop showed that several elements abundant with great variations in concentration could be studied with 5-minute time resolution.

Paper VII

The performance of the sampler described in paper VI was tested for internal losses and separation characteristics between the two size fractions.

A collision atomizer and a differential mobility analyzer were used to produce monodisperse submicron particles. A vibrating orifice aerosol generator was used to produce test aerosols consisting of larger particles.

The tests showed that the sampler was capable of collecting a separate respirable fraction in good agreement with the standard of the BMRC (British Medical Research Council) as well as a coarse fraction of which the upper particle size limit depends on the performance of the sampler inlet. The internal losses are about 5 % for particle sizes between 0.1 and 10 μm .

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On the Application of Elastic Scattering Analysis as a Complement to PIXE for the Determination of Light Elements in Thin Aerosol Samples

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ABSTRACT

The potential of elemental analysis of light elements by measuring elastically scattered particles as a complement to PIXE (Particle Induced X-ray Emission analysis), when using a 3 MV electrostatic tandem accelerator, is discussed. The discussion is based on protons and He ions with energies suitable for PIXE. Some experimental results of scattering yields are included.

INTRODUCTION

Since its introduction as an analytical method Particle Induced X-ray Emission (PIXE) (1) has been used in several studies of aerosols. The multielemental nature of the method and its capacity to give fast and reliable analysis of high sensitivity is ideal for determining low amounts of elements in large quantities of small aerosol samples.

The lightest elements cannot be analysed with PIXE due to the low energies of their characteristic X-rays. In a transition region ($12 \leq Z \leq 16$) the possibility of performing quantitative analysis is highly dependent on the sample homogeneity and the ability to determine the X-ray absorption in the sample and between the sample and the sensitive volume of the detector.

In contrast to X-ray fluorescence (XRF) PIXE offers the possibility of detecting the light elements by measuring signals originating from the nuclei of these elements. Particle Elastic Scattering Analysis (PESA)

and Particle Induced γ -ray Emission (PIGE) can be performed simultaneously with PIXE. In this paper the combined use of PESA and PIXE using protons and He-ions from a 3 MV electrostatic tandem accelerator is discussed.

ELEMENTAL RESOLUTION

By bombarding samples with protons and He ions elemental analysis can be performed by detecting particles elastically scattered. Proton energies below 1 MeV and He-ions below 2 MeV are often used. These energies are lower than the Coulomb barrier for most nuclei. Thus scattering yields can often be predicted in these cases by using the classical Rutherford formula for the differential cross-section of scattering from a point charge (2). The method is usually called Rutherford Back-Scattering Analysis (RBS) and is well established (3). By measuring the energies of the scattered particles the masses of the target nuclei can be determined using the following formula (4)

$$E_M = E_0 \left\{ \frac{m \cos \theta + \sqrt{M^2 + m^2 \sin^2 \theta}}{m + M} \right\}^2$$

θ = scattering angle in the laboratory system

m = mass of the projectile particle

M = mass of the target nucleus

E_0 = energy of the incident particle

E_M = energy of particle scattered by a nucleus with mass M

The elemental resolution is highest for light elements. The simultaneous detection of scattered particles with a surface barrier detector and X-rays with a Si(Li) detector is an attractive combination. However, for thin PIXE-samples (e.g. aerosol samples) the projectile energies used for traditional RBS-analyses are not sufficiently high for elemental resolution of the light elements which can not be analysed with PIXE. Cahill et al. (5) have detected forward scattered He ions with an incident energy of 30 MeV for the determination of elements from hydrogen to fluorine in aerosol samples. Nelson and Courtney (6) have analysed light elements in

aerosol samples by detecting protons, with an incident energy of 16 MeV, scattered 135° . For small accelerators the maximum energy available limits the thickness of the samples which can be analysed. Determinations of surface concentrations can, however, be performed without completely separated signals from the elements. Kemp (7) has used 3 MeV protons for the analysis of C, N and O in aerosol samples by comparing the concentrations of the elements in the samples with the concentrations in the aerosol filter.

To facilitate the discussion of the potential of elastic scattering analysis two scattering geometries are given in fig 1. In the arrangement shown in fig 1 a particles scattered 155° are detected with a circular surface barrier detector. This arrangement is used in the present PIXE facility in Lund (8). Figure 1 b shows an arrangement with an annular detector with a 174° scattering angle which is intended to be used in a future construction.

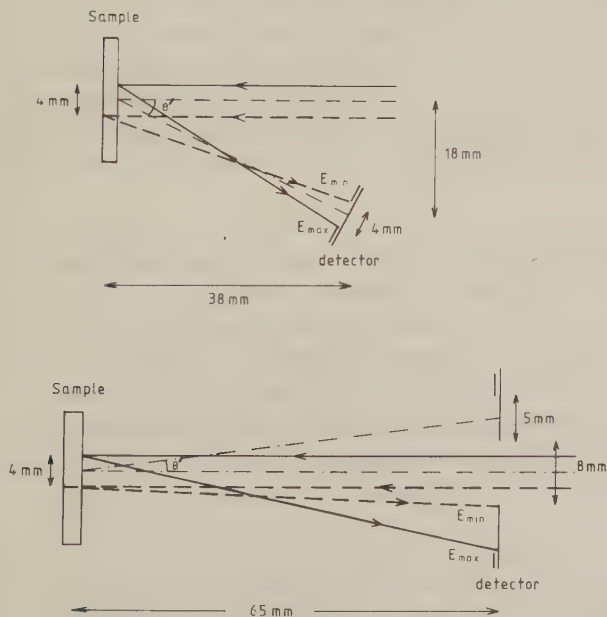


Figure 1.

Two geometrical arrangements, a) with a circular detector and b) with an annular detector, suitable for elastic scattering analysis. The solid angles are 7.2 and 48 msr in a) and b) respectively. Scattering angle = $180 - \theta$.

The annular detector covers a much larger solid angle at equal differences between maximum and minimum scattering angle ($\Delta\theta$) than the circular detector. The annular detector also detects particles in a more backward direction, making the path in the sample of the scattered particle shorter, which reduces the energy loss. With increasing scattering angle $dk/d\theta$ ($k = E_M/E_0$) decreases which gives better mass resolution for a certain range of possible scattering angles of the particles detected. The increase in dk/dM with scattering angle also contributes to a better mass resolution for more backward directions.

Figures 2a-d illustrate the resolving power for light elements at the given scattering geometries and different particle energies. In the calculations stopping power data from Andersen and Ziegler (9) were used and $\Delta\theta$ is given as the difference between the maximum and minimum scattering angle according to figure 1. For 2.55 MeV protons as projectiles (figure 2a) it is obvious that all light nuclides cannot be separated. However, these projectiles may be used for special applications when samples contain a few light elements are analysed, or for the determination of beryllium, which is a toxic metal of great hygienic interest and abundant in some working environments. The sensitivity for beryllium for 2.55 MeV protons is comparatively high (table 1). For 5 MeV protons (figure 2b) the mass resolution is improved and all elements with masses below 20 u are separated for a matrix with particle stopping corresponding to that in $200 \mu\text{g}/\text{cm}^2$ carbon.

When using He-ions the increased value of dk/dM gives a substantially increased energy difference between the elements. However this advantage is limited to very thin samples. Due to the large particle stopping the mass resolution rapidly decreases when sample thickness increases. Figure 2 d illustrates the mass resolution for He ions of 9 MeV, which is the highest energy attainable with a 3 MeV tandem accelerator. For an energy loss corresponding to $200 \mu\text{g}/\text{cm}^2$ carbon, ^{11}B and ^{12}C cannot be completely separated.

In common aerosol applications (e.g. working environments and atmospheric aerosols) the boron concentration is far lower than the carbon concentration, therefore the practical target thickness limit

is often determined by the separation between ^{14}N and ^{16}O for nuclides with mass numbers below 20. The first nuclide of interest above 20 u is ^{23}Na . To separate the signal from ^{23}Na from that of ^{24}Mg , extremely thin samples are required.

For projectiles obtainable from a 3 MV tandem accelerator the highest particle energies can give sufficient elemental resolution for masses below 20 u, at least for samples of fine particles (diameter below 2 μm).

ANALYTICAL SENSITIVITY

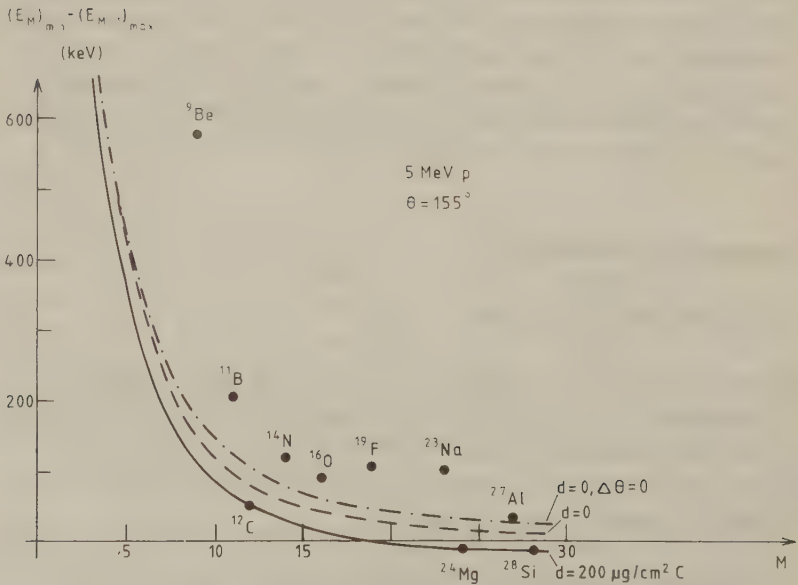
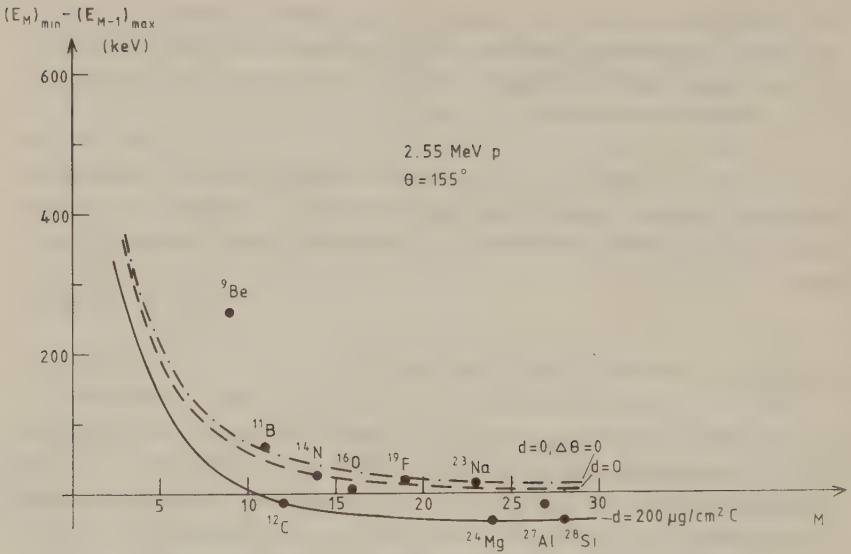
The analytical sensitivity cannot generally be predicted from existing theoretical models. However, sensitivities may sometimes be estimated from published cross section data. The differential elastic scattering cross sections of light nuclei are typically in the 1-200 mb/sr range for 2-6 MeV protons and 3-9 MeV He ions, giving analytical sensitivities between 1 and 100 pulses/ $((\mu\text{g}/\text{cm}^2) \cdot \text{msr} \cdot \mu\text{C})$. The sensitivities obtained from published data cannot normally be used for determining amounts in elastic scattering analyses. The scattering parameters used in these measurements seldom coincide with the optimal ones for analytical purposes. A useful compilation of experimental cross section data for elastic scattering and nuclear reactions has been performed by Jarjis (10).

EXPERIMENTS AND RESULTS

Estimation of sensitivities

For the estimation of analytical sensitivities thick targets can be bombarded with particles of various energies. For calibration purposes thin foils of various thicknesses have to be used. Analytical sensitivities have been estimated for two proton energies and the scattering geometry shown in fig 2a.

Protons were accelerated with an electrostatic tandem accelerator (NEC 3 UDH) to 2.55 and 5.00 MeV respectively and the scattered particles



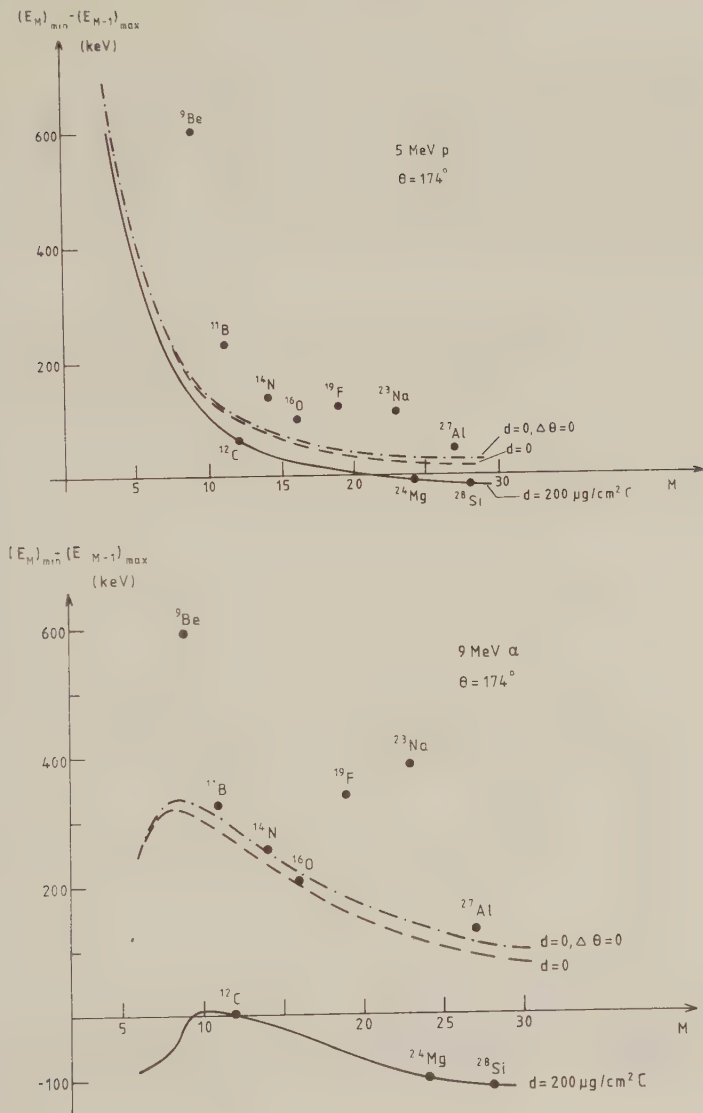


Figure 2

Illustrations of elemental resolving powers for scattering geometries shown in figure 1, and a sample thickness corresponding to 200 $\mu\text{g}/\text{cm}^2$ carbon. The solid line shows the difference between minimum and maximum energies for consecutive mass numbers. For comparison the resolution is also illustrated by curves for d (thickness) = 0 and $\Delta\theta$ (maximum difference in scattering angle) = 0. The dots show the differences between minimum and maximum energies for the major isotopes of consecutive elements (excluding neon) calculated for a sample thickness of 200 $\mu\text{g}/\text{cm}^2$. To obtain completely separated peaks $(E_M)_{\min} - (E_{M-1})_{\max}$ should be greater than 20-40 keV due to detector resolution and energy straggling.

were detected (scattering angle = 155 ± 2 , solid angle = 1.8 ± 0.1 msr) with a partially depleted surface barrier detector (ORTEC TA-014-25-300). The experimental set-up for PIXE analysis in Lund described by Malmqvist et al. (8) was used. Pellets (made of LiCl, Li_2CO_3 , H_3BO_4 , NH_4Cl , MgSO_4 and $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$), metallic foil (Be and Al) and SiO_2 were used as targets.

The sensitivities were calculated from the height of the edges in the particle spectra originating from scattering in a surface layer with thickness, δx , corresponding to a particle energy stopping, δE , of one channel width in the spectrum. The following expressions were used (3),

$$A = Q \sigma \Omega N_A t$$

$$H = Q \sigma \Omega N_H \delta x$$

$$\delta x = \frac{\delta E}{(E_M/E_0)(-dE/dx)_{E_0} + (-dE/dx)_{E_M} (1/\cos\theta)}$$

Ω = solid angle (sr)

A = number of pulses in a peak from the element in a "thin target spectrum"

Q = number of projectiles

σ = average differential cross section, (cross section for scattering (cm^2/sr))

N_A = number of atoms per cm^3 in the thin sample

t = sample thickness (cm)

$-dE/dx$ = stopping power (keV/cm)

N_H = number of atoms/ cm^3 in the thick sample

H = height of the edge in spectrum from thick samples (pulses)

and the number of pulses for a given amount of an element is calculated from:

$$A/(N_A t) = H/(N_H \delta x)$$

Stopping power data from Andersen and Ziegler (9) were used for

ELEMENT	SENSITIVITY	
	(pulses/ $(\mu\text{g}/\text{cm}^2) \cdot \text{msr} \cdot \mu\text{C}$)	
	2.55 MeV protons	5 MeV protons
Li	22	31
Be	76	11
B	42	20
C	36	42
N	23	19
O	18	25
F	3.0	3.6
Al	6.9	3.3
Si	6.5	7.6
P	7.4	20

Table 1.

The sensitivities obtained using 2.55 and 5.0 MeV protons (scattering angle = 155°) for light elements. The uncertainties are below 15%. The sensitivities for Na and Mg were below 5 pulses/ $(\mu\text{g}/\text{cm}^2) \cdot \text{msr} \cdot \mu\text{C}$.

calculations of δx . The estimations of the sensitivities are given in Table 1. For carbon, sensitivities were obtained from irradiation of thin polystyrene foils.

Evaluation of spectra from thin samples

The peaks in an elastic scattering spectrum are not gaussian. The continuum on the low-energy side of a peak has only recently been explained. With the present knowledge it is not possible,

in general, to give an analytical expression for the shape of non-Rutherford elastic scattering spectra. This makes it difficult to perform theoretical fits to experimental data points in the spectra.

To perform an evaluation of some simple methods for peak integration thin polystyrene foils spiked with cobalt were prepared (11). The foils were irradiated by 2.55 MeV protons. X-rays and scattered particles were detected simultaneously. The foils were spiked with 2060 ± 70 ppm cobalt and the thicknesses of the foils were calculated from the cobalt determination. Figure 3 shows a schematic one-peak spectrum. The magnitude of the carbon signal was determined in three different ways; a) the counts in the peak (P+B) and the low-energy continuum (T) were summed, b) the total number of counts in the peak (P+B) was found by integration and c) the number of counts in the peak corrected for a linear background was calculated (P).

Figure 4 shows the number of counts as a function of the foil thickness for the three measures of estimating the intensity of the carbon signal. In all three methods the intensity of the carbon peak increased linearly with foil thickness up to a thickness of 200 $\mu\text{g}/\text{cm}$.

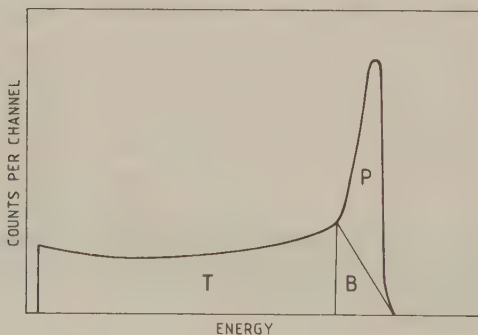


Figure 3.

A schematic one-peak elastic scattering spectrum.

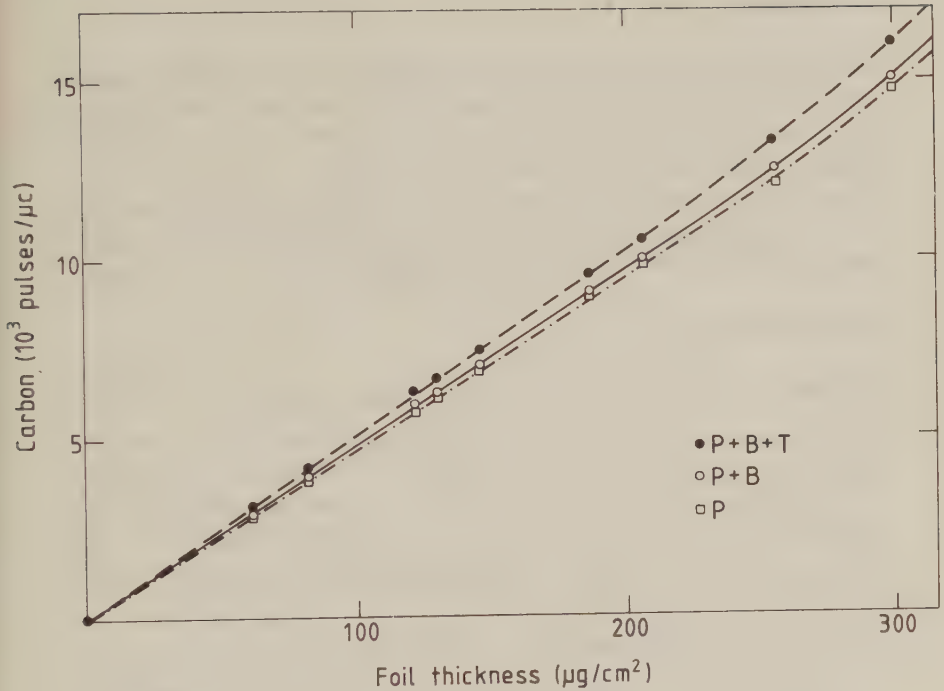


Figure 4.

Number of counts in the carbon peak as a function of sample thickness for polystyrene foils. Three different methods of estimating the number of counts in the carbon peak have been used with notations as given in figure 3.

The deviation from linearity for thicker samples is discussed in a previous paper (11). Any of the three measures can be used for a one-peak spectrum. Summation of the peak, background and tail (P+B+T) is however not applicable for spectra consisting of a number of peaks. The total counts in the peak (P+B) may be the most appropriate when the number of counts in the low energy tail is low. This can large uncertainties when B is subtracted. For spectra with low-energy tails of a considerable size, the peaks corrected for a linear background can be a better measure because this method is less sensitive to how the width of the peak is defined.

CONCLUSIONS

Protons and He ions from a 3 MV electrostatic accelerator may, to a limited extent, be used for the analysis of the light elements, simultaneously with the PIXE analysis, in aerosol samples. To obtain high elemental resolution there are restrictions on the sample thickness and particle size which can be analysed. Calibration of carbon in a polystyrene matrix shows a linear yield below 200 $\mu\text{g}/\text{cm}^2$ for 2.55 MeV protons scattered 155 degrees.

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Calibration Procedure for Particle Elastic Scattering Analysis of Thin Samples

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Abstract

A calibration procedure for particle elastic scattering analysis using simultaneous detection of X-rays and scattered particles from spiked polystyrene foils of varying thickness is described. Experimental results of proton scattering yield dependence on sample thickness are given for carbon in a polystyrene matrix.

1. Introduction

The Rutherford Back-Scattering method (RBS) is a well established technique (1) for the analysis of thin films, determinations of surface compositions and studies of elemental depth profiles in surface layers of bulk samples. The samples are usually bombarded with low energy protons (< 1 MeV) or He-ions (< 2 MeV). The simultaneous detection of scattered particles with a surface barrier detector constitutes an attractive complement to Particle Induced X-Ray Emission (PIXE) analysis for the determination of light elements. However, even for thin PIXE-samples (e.g. aerosol samples) the projectile energies used for traditional RBS-analyses are not sufficiently high for elemental resolution of the light elements which can not be analysed with PIXE. With increasing projectile energy the classical Rutherford scattering formula ceases to be valid, making predictions of the differential cross sections difficult. In this paper a calibration technique for high precision analysis of thin samples is described.

2. Calibration procedure

2.1. Simultaneous detection of X-rays and scattered particles

Thin calibration standards are required for high precision analysis. To study matrix effects it is necessary to use standards of varying thickness. Using a well calibrated PIXE set-up the calibration procedure is facilitated by the simultaneous detection of X-rays and scattered particles. The standard foils can be spiked with a metal to a known concentration and the thickness, of the part of the standard foil irradiated, can be determined with high precision by PIXE analysis.

2.2. Preparation of thin standards

Preparation of spiked foils for calibration of X-ray analysis has been described earlier by Dzubay and Lamothe (2) and Billet et al. (3). In selecting material for the thin standards used for calibration several factors have to be considered. The composition must be suitable for both PIXE and elastic scattering analysis, and the levels of impurities must be low. Polystyrene is a polymer of carbon-hydrogen composition which fulfills these requirements. It also has good mechanical strength, and can easily be made into thin foils of varying thickness.

The thin polystyrene foils are prepared from a bulk solution consisting of polystyrene dissolved in toluene (4). The concentration used was 100 g polystyrene in 1 l of toluene.

A clean glass plate was partially immersed in a vertical position into the solution, and then slowly raised out of the solution, whereby the glass plate was coated with a thin film of polystyrene solution. The thickness of the film was varied by changing the speed with which the glass plate was removed. This was achieved by connecting the glass plate, by means of a cord coupling, to a syringe pump motor with variable speed. After allowing the film on the glass plate to dry, the plate was lowered at an angle into a shallow beaker of water. The water wets the surface of the glass plate thus separating the

polystyrene film from the plate.

The bulk polystyrene matrix is spiked with a known amount of a metal that is easily measured by PIXE, in this case cobalt. Since the ratio of cobalt to carbon is given by the composition of the solution, the values for cobalt can be used as calibration for the elastic scattering analysis.

In order to give good pulse counting statistics, it is desirable that the cobalt concentration be rather high. A cobalt concentration of 1 800 ppm in the resulting polystyrene foils was chosen.

The polystyrene solution was spiked in the following way. A standard solution containing 1 g Co in 1000 ml of water was prepared. To this solution 4 g DDDC (diethylammonium diethyldithiocarbamate), a complexing agent, were added causing the formation of a metal-carbamate complex. After evaporation of the water, the dry metal complex, which is soluble in toluene, was added to the polystyrene solution.

Thin foils may be spiked with light elements in the same way by spiking a polystyrene solution with known amounts of the element in the form of a toluene-soluble compound.

The foils have been prepared in thicknesses varying from 20 to 1000 $\mu\text{g}/\text{cm}^2$. The limiting factor is the mechanical strength of the foils. When the thickness is less than about 20 $\mu\text{g}/\text{cm}^2$, the foils are very fragile and almost impossible to handle with our techniques.

2.3. Calibration

Calibrations for carbon analysis were carried out by irradiating the spiked polystyrene foils with protons of 2.55 and 5.00 MeV. The protons were accelerated with an electrostatic tandem accelerator (NEC 3 UDH). The PIXE set-up for routine analysis at the Lund Institute of Technology described by Malmqvist et al. (5) was used. The angle between the beam and sample normal was 22.5° and a partially depleted surface barrier detector (ORTEC TA-014-25-300) collimated to 3.1 mm^2 was placed under the beam for the detection of protons scattered 155° .

in a solid angle of 1.8 ± 0.1 msr. The number of Co K_{α} pulses in the X-ray spectrum, multiplied by a thick target correction factor (6), is a measure of the foil thickness. Figure 1 shows the number of pulses in the carbon peak of the particle spectrum as a function of the corrected number of pulses in the Co K_{α} peak. For increasing target thickness there are obvious departures from linearity. The intensity of scattered particles from carbon reaching the detector was calculated by summing the number of pulses in the characteristic carbon peak without any correction for the background on the low energy side of the peak. Figure 2 shows the particle spectrum for a $30 \mu\text{g}/\text{cm}^2$ spiked polystyrene foil.

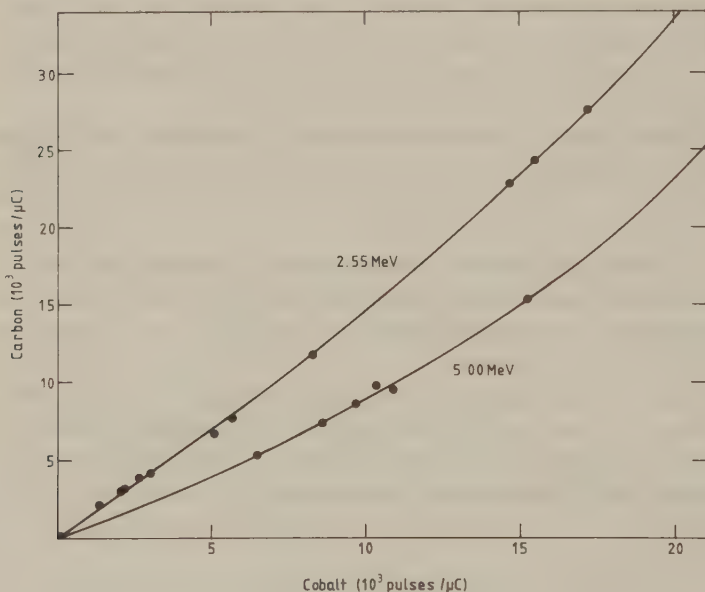


Figure 1.

Relation between carbon pulses/ μC (A) and cobalt K_{α} pulses/ μC (N) from the simultaneous detection of scattered particles and X-rays according to the calibration procedure described in the text. For 2.55 MeV and 5 MeV protons 33 ± 2 and 62 ± 3 pulses/ μC respectively correspond to $1 \mu\text{g}/\text{cm}^2$ polystyrene. The cobalt concentration in the polystyrene was 1785 ± 60 ppm. The particles were scattered 155 ± 2 into a solid angle of 1.8 ± 0.1 msr. The solid lines represent the functions $A = 1.35N + 6.9 \cdot 10^{-8} N^{2.55}$ (2.55 MeV) and $0.75N + 8.7 \cdot 10^{-8} N^{2.55}$ (5.00 MeV). The uncertainties due to counting statistics are below 1%.

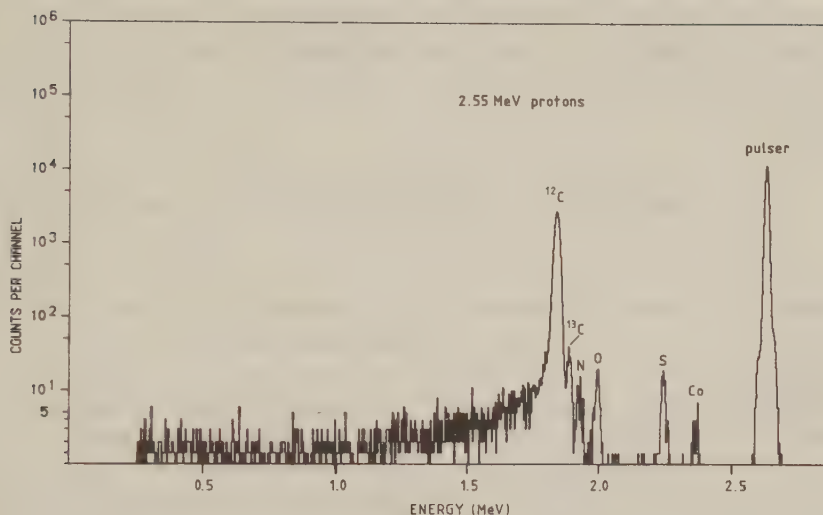


Figure 2.
Particle spectrum from a spiked polystyrene foil with thickness $30 \mu\text{g}/\text{cm}$. The foil was irradiated with $10 \mu\text{C}$ protons and the scattered particles were detected at a scattering angle of 155° and into a solid angle of 1.8 msr . Sulphur and nitrogen are constituents of the DDDC-compound ($\text{C}_3\text{H}_{22}\text{N}_2\text{S}_2$).

3. Discussion

A peak in an elastic scattering spectrum does not have a gaussian shape and cannot easily be fitted by theoretical models in the case of non-Rutherford scattering. The low energy tail and the background continuum behind the peak have been of unknown origin (1). However, recently Weber et al. (7, 8) have successfully performed computer simulations of RBS-spectra assuming that the low-energy continuum is due to multiple scattering (mainly double scattering) in the sample. Usually in particle elastic scattering analysis the elements are quantified by simply summing the pulses in the characteristic peak.

However, the lack of knowledge about the magnitude of doubly-scattered particles in relation to singly-scattered particles may cause a significant analytical error. Weber and Mommsen (8) give a quantitative measure of the number of doubly-scattered particles in an RBS-spectrum:

$$\text{Bkgnd} = \text{const} \cdot f(E, \theta, Z) \cdot d^{2.55}$$

Bkgnd is the number of particles doubly-scattered into a certain solid angle and into an energy interval of the spectrum. $f(E, \theta, Z)$ is a function, of energy (E) of the incident protons, scattering angle (θ) and atomic number (Z) of the target nucleus, valid for classical RBS and d is the target thickness. The proton energies used in the carbon calibration procedure are beyond the valid region of their formula. The $d^{2.55}$ -dependence, however, is a geometrical factor and can be assumed to be independant of energy. In figure 1 our experimental data are fitted to a function $A = aN + bN$ (A= number of pulses in the carbon peak, N= number of pulses in the Co K_{α} -peak and a measure of the target thickness; a and b are constants) which seems to describe the experimental results.

The additional $d^{2.55}$ -dependence indicates that a significant number of doubly-scattered particles were included when the total number of counts in the characteristic peak was calculated.

4. Carbon analysis

In the analysis of aerosol samples carbon is an element of considerable interest. The foils used for calibration can be used as aerosol collection substrates. Since they have a well determined ratio between the metal and the carbon content, the substrate content of irradiated carbon may be subtracted from e.g. an impactor sample with a fine aerosol fraction. Andreae and Barnard (9) have described a similar technique using the constant ratio between carbon and fluorine in a teflon filter. Figure 3 shows an example of carbon analysis using scattered He-ions on a silver membrane filter for aerosol collection. Figure 4 shows an example of proton elastic scattering analysis of

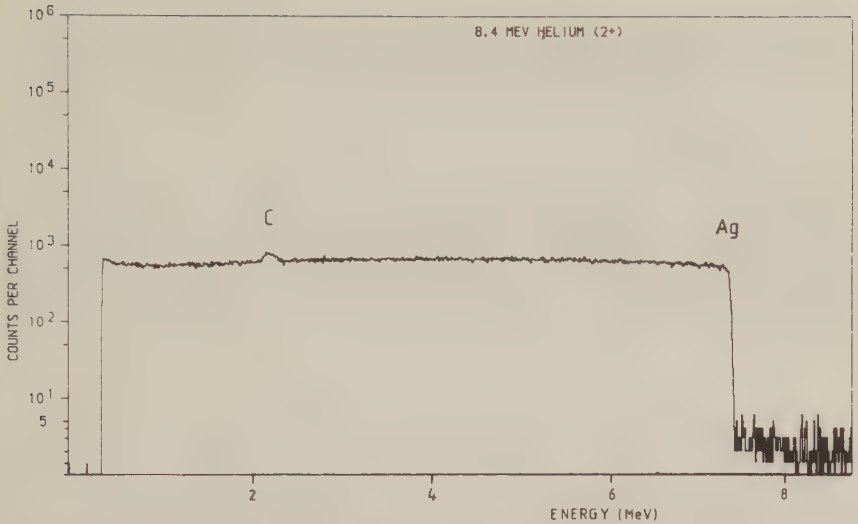


Figure 3.

Particle spectrum from a silver membrane filter coated with $20 \mu\text{g}/\text{cm}$ carbon. The filter was irradiated with $4.4 \mu\text{C}$ He^{+} ions and the scattered particles were detected at a scattering angle of 155° and into a solid angle of 2.8 msr .

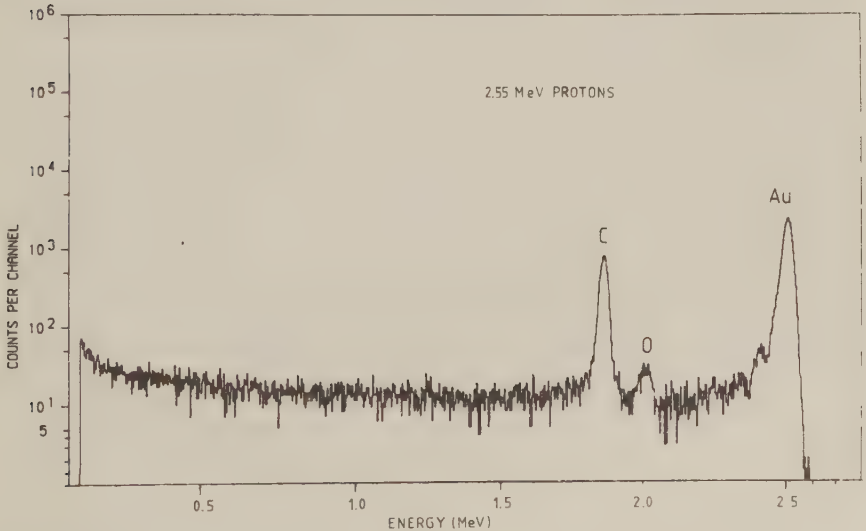


Figure 4.

Particle spectrum from a gold foil coated with $20 \mu\text{g}/\text{cm}$ carbon. The foil was irradiated with $2.6 \mu\text{C}$ protons and the scattered particles were detected at a scattering angle of 155° and into a solid angle of 2.8 msr .

carbon on a gold foil. The two substrates were coated with $20 \mu\text{g}/\text{cm}^2$ carbon.

5. Conclusions

For elastic scattering analysis of high precision careful calibration with standards of varying thickness has to be performed. By using thin plastic foils spiked with a metal together with simultaneous X-ray and particle detection the calibration procedure is facilitated.

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PIXE DETECTION LIMITS FOR SOME AEROSOL COLLECTION SUBSTRATES BY EXCITATION WITH PROTONS AND He^{++} -IONS FROM A 3 MV TANDEM ACCELERATOR

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Abstract

Comparisons of PIXE detection limits for K_{α} X-rays using 2-5 MeV protons and 7-8 MeV He^{++} -ions as projectiles have been performed. The comparisons have been made for common aerosol backings. According to simple theoretical considerations regarding X-ray production cross sections and the production of background radiation, detection limits for He^{++} should be 2-4 times lower than for protons for equal velocity projectiles of equal numbers. However, the background in X-ray spectra arising from γ -quanta being Compton-scattered in the Si(Li)-detector can strongly effect the detection limits. The detection limits using protons and He^{++} -ions from a 3 MV electrostatic tandem accelerator are determined and discussed.

1. Introduction

Through the years PIXE has developed many different approaches to the problem of obtaining low detection limits for a specific sample of interest. This paper deals with the suitability of using He^{++} as a projectile instead of the more commonly used proton for production of K_{α} -radiation. It is not possible to analyze the lightest elements with PIXE, a draw-back that can be overcome in various ways. In PIGE the induced γ -rays may be detected simultaneously with the X-rays, and Particle Elastic Scattering Analysis (PESA) uses the back-scattered projectiles to determine the amounts of the low-Z-elements. As the mass resolution of PESA for very thin samples increases with the mass of the projectile, a combined measurement of both X-rays and back-scattered He^{++} -projectiles could be a better alternative than using protons as projectiles for simultaneous analysis of all elements

(except hydrogen and helium). The γ production yield is usually higher when He^{++} is used as the projectile thus making He^{++} -ions more advantageous than protons for PIGE^{1,2,3)}.

The minimum detection limits are in this paper defined as $3(N_b)^{1/2}/S$, where N_b is the number of pulses within an interval of two full widths at half maximum around the K_α -peak. If $N_b < 11$, then $3(N_b)^{1/2}$ is set to 10. S is the sensitivity, or the K_α -yield, measured in (number of K_α -counts per projectile / mass per sample area). The sensitivity S decreases rapidly with increasing Z due to the fact that the production cross section for K_α -radiation $\sigma_p = \sigma_{\text{ion}}^{wk}$ is a steadily declining function of Z in the relevant Z interval. According to BEA-calculation⁴⁾, the production cross section using He^{++} as projectile is four times higher than for protons, for equal velocity projectiles. Thus, S becomes four times larger, hinting a possibility of improved detection limits. Another approach is to use a higher projectile energy, as σ_p increases with increasing energy of the projectile for the energies in question. Doing this one must keep in mind the effect of these parameters on the counter-balancing factor N_b .

The background radiation comes mainly from secondary electron bremsstrahlung, projectile bremsstrahlung and Compton-scattered γ -quanta. The secondary electrons give the main contribution to the background up to the energy $T_m = 4m_e E / (M_p A)$, where m_e and M_p is referring to the electron and proton mass, and E and A is the projectile energy and mass number. This usually corresponds to energies of characteristic K_α -radiation for elements in the region $Z=30$. The γ -quanta that are Compton-scattered in the Si(Li)-detector give rise to a very slowly decreasing background level above T_m , and determine the background level at these energies. The projectile bremsstrahlung is in a first approximation⁵⁾ proportional to $(Z_t/A_t - Z_{\text{proj}}/A_{\text{proj}})^{1/2}$, suffix t and proj referring to the target and the projectile respectively. As most elements have a Z/A ratio of around 1/2, this term should be considerably lower when using He^{++} as projectiles instead of protons. The design of the experimental chamber is also of importance when trying to reduce the background radiation.

A complete theoretical evaluation of the detection limits using different projectiles at different energies on many different backings would indeed be a formidable task. It is necessary to make experiments on which to base further discussion on the subject.

2. Experiment and results

All experiments were made at the 3 MV tandem accelerator laboratory (NEC 3 UDH) with adjoining PIXE set-up at the Lund Institute of Technology, Sweden. The set-up is described in detail by K.G. Malmqvist et al.⁶⁾. The X-rays produced are detected in an 80 mm² (collimated to an effective area of 28 mm²) Si(Li) Kevex detector with an energy resolution of 158 eV at 5.9 keV. The detection was made at an angle of 135 degrees to the projectile beam, through a 109 μ m Be chamber window, a 4 mm air gap and a 25 μ m Be detector window, at a total distance of 4 cm from the sample. Simultaneously, the γ -radiation was detected at a 90 degree angle using a Ge(Li) detector. This was done to make it easier to evaluate the effect of the γ -radiation on the X-ray spectra. The charge was measured with an Ortec Model 439 Current Digitizer.

Four different non-exposed backings were bombarded: Polystyrene, Kimfol, Nuclepore and Teflon. The Polystyrene film was made in our laboratory and has an estimated thickness of 0.03-0.04 mg/cm². This very thin and delicate foil is well suited for different chemical analyses demanding high purity backings. Kimberley-Clark's Kimfol backing is about 0.2 mg/cm² thick and is a polycarbonate. Nuclepore (also a polycarbonate) is approximately 1 mg/cm² thick and often used as an aerosol collection substrate. The last backing; Millipore's commonly used Teflon filter Fluoropore FHUP is about 2 mg/cm² thick. The difficulty with Teflon is that it is polytetrafluoroethylene, containing fluorine as a constituent of the foil. This give rise to many γ -transitions from fluorine, causing a distinct increase of the background level in the X-ray spectra.

As the Lund PIXE group regularly uses 2.55 MeV protons for their analyses, the design of the experimental chamber has been adapted to this energy with regard to background yield. When running the proton experiments no changes were made in the chamber, but when He⁺⁺ was used as projectile a Ni collimator (6.5 mm diameter) was placed 29 cm before the target, covering the 8 mm diameter carbon collimator and defining the beam (fig. 1). The choice of Ni as collimator material was based on the work by Giles and Peisach³⁾ indicating the absence of ($\alpha, \alpha'\gamma$) reactions when using 5 MeV He⁺⁺ as projectiles. The revolving set of carbon collimators situated between the target and the Ni collimator was then turned to its maximum diameter collimator (13 mm diameter), thus preventing the beam from hitting any carbon directly.

By doing this the otherwise very intense 4.4 MeV γ -rays from the $^{12}\text{C}(\alpha, \gamma)^{12}\text{C}$ reaction completely disappeared in the γ -spectra.

The ionization cross sections used in the calculations of the detection limits were those derived from Akselsson/Johansson's fifth-degree polynomial⁷⁾. According to BEA theory the cross sections scale as the square of the ratio between the charge of the different projectiles, for equal velocity projectiles. It means that, comparing protons with He^{++} , the ionization cross sections are four times higher using He^{++} with four times the kinetic energy of the proton. This was used when estimating the ionization cross sections for He^{++} , as the fifth-degree polynomial was calculated from proton data only. Deviations from the assumed scaling will cause a systematic error in the detection limits for He^{++} given here.

All the detection limits are given in the unit (ng per cm^2 sample area / $2.5 \cdot 10^{14}$ projectiles), using no external absorber. For the 5 MeV proton run and the both He^{++} -runs we actually used a 340 μm Mylar absorber, but the detection limits were afterwards corrected to zero absorber. The number of $2.5 \cdot 10^{14}$ projectiles represents a collected charge of 40.0 μC for protons and 80.0 μC for He^{++} . The detection limits are valid for low-loaded backings. The detection limits for an equal amount of charge instead of projectiles (e.g. 40.0 μC) will be obtained by multiplying the He^{++} values by the square root of 2, for $N_b > 11$. If the limiting factor is the beam current causing an excessive heating of the sample, a normalization to the energy deposited in the sample should be more appropriate. Bethe-Bloch's formula for the stopping power shows that the energy deposition in the backing is approximately four times higher for He^{++} than for protons for projectiles of the same velocity. The effect on the detection limits is a factor 2 to the advantage of the protons.

The amount of charge being allowed to hit the target was determined by pulse statistics and time consideration. This meant a charge of 100 μC for the protons and 25-70 μC for He^{++} , except for Teflon which gives fully adequate pulse statistics after as little as 5 μC . The maximum uncertainty in the pulse statistics is 30 %. This value comes from the fact that if $N_b < 11$, the value of $3(N_b)^{1/2}$ is set to 10, which is sometimes the case for $Z > 30$. Another contribution to the statistical error arises when the number of pulses in the background below two full widths at half maximum (FWHM) is determined. This contribution to the uncertainty of the determination of the detection limits is less than 20 %. We assume that the FWHM is proportional to $(\alpha + \beta E)^{1/2}$, E indicating the K_α -energy. α and β are constants that are determined experimentally.



Figure 1: The experimental chamber. The 6.5 mm Ni collimator was covering the 8 mm carbon collimator at a distance of 29 cm before the target.

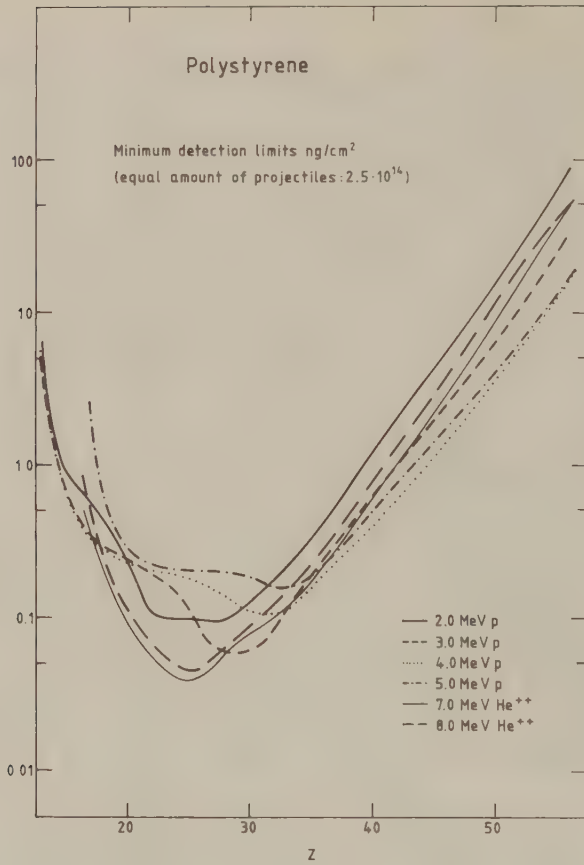


Figure 2: Minimum detection limits in (ng per cm² sample area / $2.5 \cdot 10^{14}$ projectiles) for 2,3,4 and 5 MeV protons and 7 and 8 MeV He⁺⁺ on POLYSTYRENE.

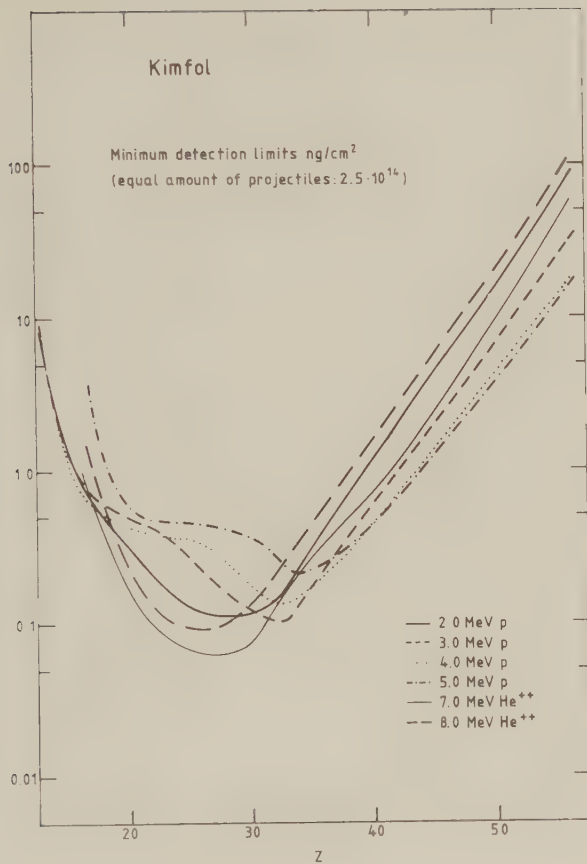


Figure 3: Minimum detection limits in (ng per cm² sample area / $2.5 \cdot 10^{14}$ projectiles) for 2,3,4 and 5 MeV protons and 7 and 8 MeV He⁺⁺ on KIMFOL.

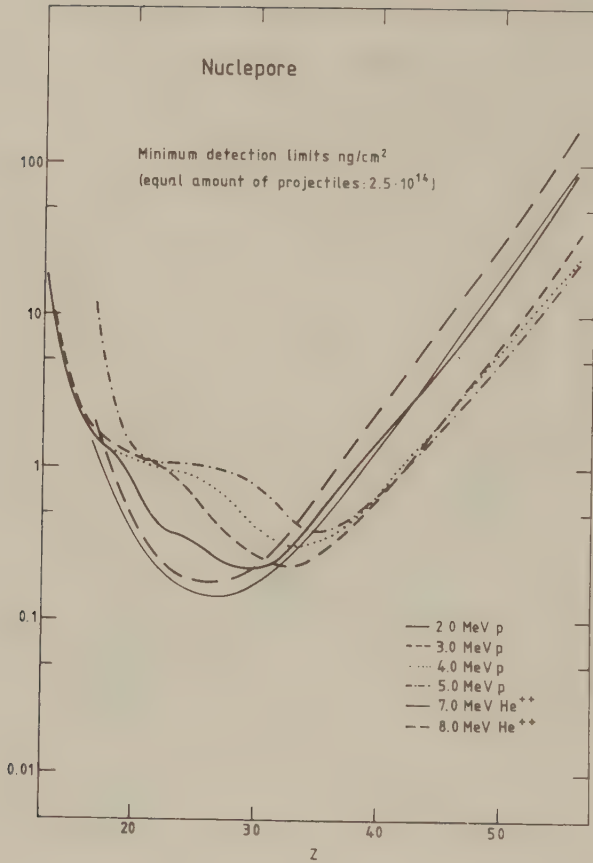


Figure 4: Minimum detection limits in (ng per cm² sample area / $2.5 \cdot 10^{14}$ projectiles) for 2,3,4 and 5 MeV protons and 7 and 8 MeV He⁺⁺ on NUCLEPORE.

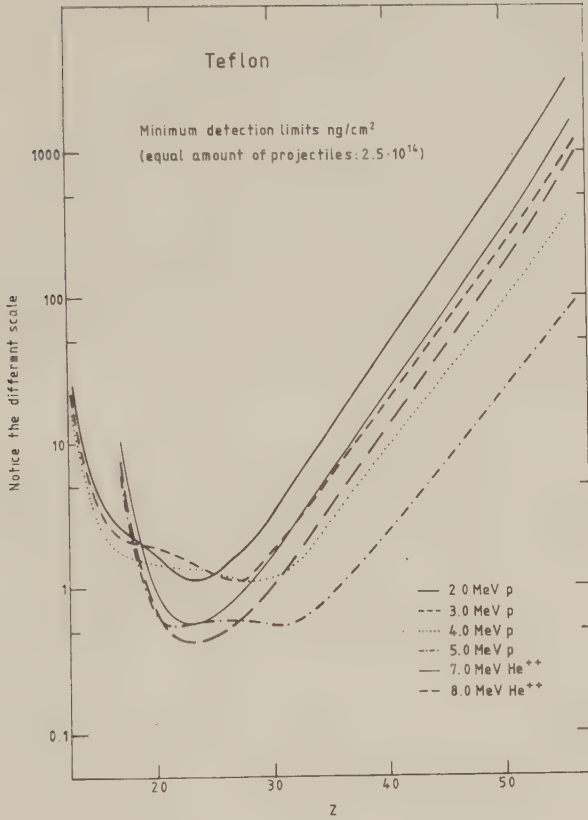


Figure 5: Minimum detection limits in (ng per cm² sample area / $2.5 \cdot 10^{14}$ projectiles) for 2,3,4 and 5 MeV protons and 7 and 8 MeV He⁺⁺ on TEFLON. Notice the different scale.

Minimum detection limits have thus been calculated for 2,3,4 and 5 MeV protons and 7 and 8 MeV He^{++} -ions on four backings; Polystyrene, Kimfol, Nuclepore and Teflon. This gives us 24 curves presented in four diagrams, one for each backing (fig. 2-5). Notice the different scale in the Teflon diagram. The curves stretch from Cl to Ba ($Z=17-56$), and in the case of 2,3 and 4 MeV p all the way from Al ($Z=13$).

7 MeV He^{++} -ions give the lowest detection limits in the region $Z=18-31$ (except for Teflon) of all examined projectiles and energies. For $Z>31$ protons give lower detection limits, with 4 and 5 MeV protons being superior for $Z>35$. When using the high energy protons, this shows us that the higher background continuum in this region isn't enough to make up for the increase in production cross sections. Below T_m this advantage is lost for 4 and 5 MeV protons, making 2 and 3 MeV protons more suitable. The minimum is shifted towards higher Z using higher proton energies due to the direct effect of the projectile energy on T_m . For He^{++} at only two different energies this is not noticeable.

3. Discussion and conclusions

A closer study of the curves gives an impression that the optimum proton energy should lie somewhere around 3 MeV for K_α -radiation, giving us low detection limits both in the low- and high- Z region. The He^{++} -energy of preference would be 7 MeV or lower, as the detection limits at this energy is lower than for 8 MeV He^{++} (except for Teflon). The choice of energy is to some extent dependent on the purpose of the analysis. Studying aerosol samples one is often interested in low- Z elements such as sulphur, motivating a somewhat lower energy. When looking at pollutants in an industrial environment high- Z elements like cadmium are often looked for, suggesting a higher optimum projectile energy. When establishing an experimental set-up for extensive routine PIXE analyses a compromise must be made when choosing the energy and projectile.

Figure 6 shows the ratio between the detection limits for 2 MeV protons and 8 MeV He^{++} -ions for an equal number of projectiles. A value >1 means that the detection limits are greater using protons instead of He^{++} -ions. 2 MeV protons and 8 MeV He^{++} -ions have the same velocity, and the production cross sections for He^{++} should be therefore four times larger than those of protons according to the BEA scaling rule. Knowing that the definition of the detection limits is $3(N_b)^{1/2}/S$, it can be assumed as a first rough estimate that the ratio between the detection limits of 2 MeV protons and 8 MeV He^{++} -ions

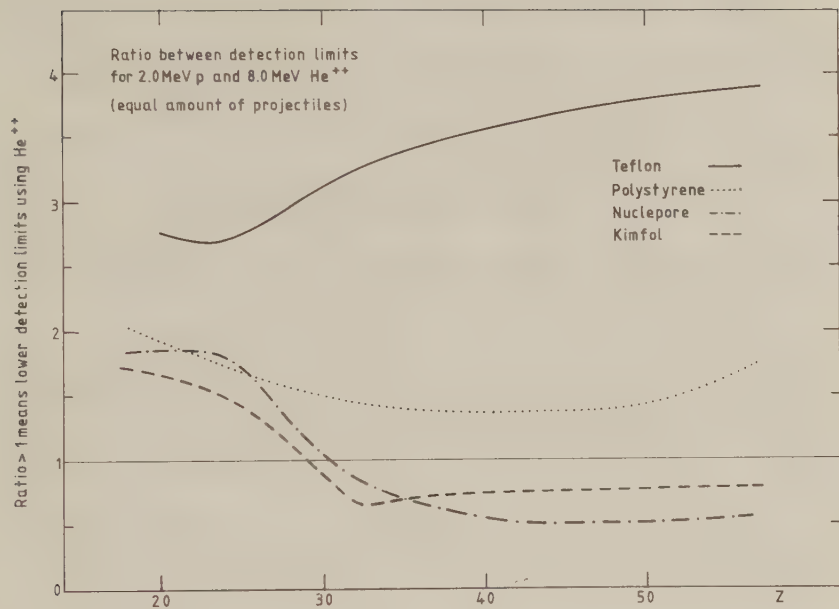


Figure 6: Ratio between the detection limits for 2 MeV protons and 8 MeV He^{++} (equal velocity projectiles) for equal numbers of projectiles.

should be about 2 below T_m and 4 for high Z . As can be seen in the figure this is hardly the case. For Kimfol and Nuclepore the ratio is even below 1 above Cu ($Z=29$). This could be explained by the increased γ -radiation emanating mainly from the sample itself, which is then Compton-scattered in the Si(Li) detector. Notice that the value 2 for the ratio below T_m agrees better with the data in figure 6, probably because here the Compton background is not the determining factor.

7 MeV He^{++} -runs with carbon collimators instead of the Ni collimator indicate that the detection limits are increased by some 10 % due to the intense 4.4 MeV γ -radiation from the carbon. The question arises if the experimental chamber could be further improved. Scattering of projectiles by the target, subsequently causing the projectiles to hit the chamber walls, may give rise to an increased X-ray background that perhaps could be avoided. A study of this will be the object of further investigations.

In conclusion, the detection limits using 7 and 8 MeV He^{++} -ions as projectiles are of the same order and in many cases ($Z=18-31$) lower than those using 2,3,4 and 5 MeV protons for equal numbers of projectiles. The choice of projectile and projectile energy must be a compromise between the low- and high- Z detection limits. Complementary methods such as PIGE and PESA for the detection of low- Z elements should also be taken into consideration. The design of the experimental chamber should be made with some care when using He^{++} as projectile, in order to reduce the high intensity Compton-scattering of γ -radiation in the Si(Li) detector, causing an increased background in the X-ray spectra.

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AN ANALYTICAL PROCEDURE FOR DETERMINING CHROMIUM IN SAMPLES OF AIRBORNE DUST

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Abstract—A method is described for assessing occupational exposures to chromium aerosols; it involves four procedures. The first, proton induced X-ray emission (PIXE), measures the total chromium. The second, electron spectroscopy for chemical analysis (ESCA), measures the oxidation state of the particle surfaces, and the third, which uses sym-diphenylcarbazine (DPC), measures the proportion of water-soluble chromium VI. The fourth, transmission electron microscopy (TEM), provides information about the size and shape of the particles and guides the interpretation of the ESCA-data.

The multi elemental nature of PIXE-analysis is advantageous in eliminating the possibility of interference in the DPC-method and in eliminating chromium compounds from the tentative list of existing health hazards in the smoke. These methods were applied to the analysis of samples of fume produced in welding, and information was obtained for the amounts of soluble and insoluble chromium (III and VI) in samples of different aerosols.

INTRODUCTION

EXPOSURE to chromium compounds constitutes a health hazard to workers in a number of different occupations. Ulcerations, dermatitis and respiratory cancers have been reported and the damage seems to depend on the oxidation state of the chromium and on the solubility of the particular compound involved, e.g., certain less water-soluble chromium (VI) compounds may be carcinogenic (NATIONAL INSTITUTE OF OCCUPATIONAL SAFETY AND HEALTH (NIOSH), 1975; HUNTER, 1976; HEALTH AND SAFETY EXECUTIVE (HSE), 1977; AMERICAN CONFERENCE OF GOVERNMENTAL INDUSTRIAL HYGIENISTS (ACGIH), 1977). Hence in analysing the chromium contents of particles in work environments and for assessing the harmful effects of chromium exposure, it is useful to have an analytical tool capable of giving accurate information about oxidation states and solubility.

The common methods used for chromium analysis are atomic absorption spectroscopy (AAS) and colorimetry with sym-diphenylcarbazine (DPC). A variant of the DPC method (ABELL and CARLBERG, 1974) is recommended by NIOSH (1975). With these methods, although the total amount of chromium and the soluble chromium (VI) may be determined, no information is provided about the oxidation states of the insoluble chromium fractions. The procedure for analysing samples of airborne particulates reported here is capable of separating the different oxidation states of chromium and also soluble from less soluble chromium. The results of an investigation of samples of particles generated in welding operations in stainless steel are included.

METHODS

Particles are sampled on membrane filters and analysed with proton induced X-ray emission (PIXE), electron spectroscopy for chemical analysis (ESCA) and

transmission electron microscopy (TEM) before and after washing in buffered water. After washing, the particles are considered to roughly resemble particles deposited in the lungs.

Elemental analysis

PIXE is a fast, reliable method for multielemental analysis with low detection limits (0.1–10 ng in routine analysis). For elements lighter than sulphur it is not quantitative. There are, however, a number of complementary methods which are capable of detecting several of these elements when used simultaneously with PIXE analysis. A review of the PIXE method has been published recently (JOHANSSON and JOHANSSON, 1976).

PIXE may be replaced by X-ray fluorescence (XRF) with only minor disadvantages, such as increased sample size and increased time of analysis. Atomic absorption spectroscopy (AAS) may also be used for the elemental analysis, but the capability of multielemental analysis is abandoned.

Oxidation state

The oxidation state of the chromium on the surfaces of the particles is studied by ESCA (SIEGBAHN *et al.*, 1967). The sample is bombarded with monoenergetic X-rays which induce outer electrons to leave atoms; the energies of these electrons yield information about the oxidation states on the surface. We have used aluminium K X-rays for excitation and an electrostatic electron spectrometer (AEI ES 200) for analysis of the energies of the ejected $2p_{3/2}$ electrons. For this study, standards with different ratios of Cr(VI)/Cr (total) have been prepared and analysed, giving an absolute accuracy of 0.1 and a detection limit of about 0.2 for the ratio Cr(VI)/Cr(total). Both the accuracy and the detection limit could be improved by using equipment capable of higher resolution. Because electrons ejected from the interior of the sample interact with other electrons on their way out, only a thin surface layer (about 2 nm) can be analysed. For very small particles and for particles consisting of aggregates of small identical particles the surface concentration is representative of the entire volume. For particles with diameters $<0.01\ \mu\text{m}$ ESCA is valid for more than 80% of the particle volume assuming spherical symmetry, whereas for particles with diameters $<1\ \mu\text{m}$, ESCA is valid for less than 1% of the volume.

Size and density

The transmission electron microscope is a versatile tool for studying the properties of individual welding fume particles (FRISMARK *et al.*, in press). From TEM information it is possible to estimate the representativeness of the ESCA data from the sizes of the particles and their density variations. The electron microscope used in this study was a Philips EM 300; an accelerating voltage of 100 kV gave a suitable transmission of electrons through the welding smoke samples used.

Solubility

The microenvironment encountered by particles deposited in the lungs is not fully understood. In this work a crude washing procedure, using a buffered water solution ($\text{NH}_4\text{NO}_3/\text{NH}_4\text{OH}$) at a pH of about 7.4 was employed. In the Tables below the

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'soluble' mass of an element denotes the mass leached out of the particles with the washing procedure used and dissolved in the buffered solution. The concentration of water soluble chromium (VI) is analysed by the DPC method, in which sym-diphenylcarbazine forms complexes with water soluble chromium (VI), inducing a red-violet colour (SANDELL, 1959). The absorbance is measured with a spectrophotometer. The accuracy of this method is in the order of 5% for concentrations of Cr(VI) higher than 0.05 $\mu\text{g/ml}$. Allowance may have to be made for interference. In this investigation we have used a Perkin Elmer spectrophotometer and the absorbance was measured at a wavelength of 540 nm.

Filters

For evaluation of health effects, the respirable fractions of the airborne particulates are of special interest. Cyclone samplers (Casella personal samplers) have been used to collect the respirable fraction according to the Johannesburg convention (ORENSTEIN, 1959) on membrane filters. The cyclones require a flow rate of 1.9 l./min, which is too high for small pore size filters, which are necessary for surface deposition. The particles which penetrate into the filter are not seen by ESCA or TEM analysis.

For most applications a pore diameter of 0.025 μm is recommended. To simulate particle capturing in the nose and the upper respirable tract, an impactor stage with a 50% cut-off diameter of about 5 μm may be used instead of a cyclone.

If only the total filter-sample area were considered, one filter would be sufficient for the analysis suggested. However, the washing procedure is more conveniently applied to a whole filter than to a piece of a filter, thus it is feasible to use two parallel filters. In this investigation, samples have been collected on four filters (A, B, C and D) for each aerosol. Filters A and B—for PIXE analysis and ESCA—were membrane filters of mixed cellulose esters, of 0.8 μm pore diameter and of 37 mm diameter (Millipore AAWP 03700), allowing cyclone prestages to be used. The filter efficiency for the welding aerosol is estimated from SPURNY and LODGE (1972) to be almost 100% at a flow rate of 1.9 l./min. There is a minimum in the efficiency curve at about 0.7 μm diameter, but, even at the minimum, the efficiency exceeds 95%. The decrease of the PIXE sensitivity due to penetration into the filter is insignificant for the elements concerned in this work. For ESCA, a fraction of particles in the range of 0.7 μm diameter is lost into the filter. However, the welding particles are composed of aggregates of smaller spherical particles of uniform size, thus the Cr(VI)/Cr(III) ratio is not expected to be altered by this loss. When necessary, the uncertainty due to filter penetration should be avoided by applying 0.025 μm pore-size filter and an impactor stage.

Filters A and B are employed in parallel and are weighed before and after the sampling to check their comparability. Filter B is washed in the buffered solution. Each filter is then divided into two pieces—one for PIXE (pieces A1 and B1) and one for ESCA (pieces A2 and B2).

The thickness of the loadings of filters A and B is limited by charged-particle energy loss and by X-ray absorption in the PIXE analysis and should be less than 1 mg/cm^2 for the quantitative analysis of elements as light as sulphur. The lower limit to the thickness is determined by the decreasing accuracy in gravimetric determinations. For welding fumes a thickness of 50–100 $\mu\text{g/cm}^2$ is sufficient.

Filters C and D for the TEM analysis are also employed in parallel. A thin layer of carbon is evaporated on these filters before exposure. After exposure, filter D is washed and a second layer is evaporated on both filters C and D. The filter material is dissolved and a piece of the carbon-carbon sandwich is attached to a grid for TEM analysis of the particles. In this investigation 25 mm diameter filters of mixed cellulose esters with a pore diameter of 25 nm (Millipore VSWP 02500) have been used and they were dissolved in ethyl acetate.

The results of the PIXE analyses of pieces A1 and B1 give the total mass and the less soluble fraction respectively of all elements heavier than phosphorus. This information is relevant to the health hazard assessment; it is also used to evaluate possible interferences occurring in the ESCA and DPC analyses and to derive upper limits to the amounts of certain chromium compounds. The ESCA data from filters A2 and B2 give the ratios between Cr(VI) and total chromium on the surface of the unwashed and washed particles respectively.

WELDING FUME

Welding on stainless steel often produces high concentrations of chromium in the breathing zone. The fumes generated in welding with three different kinds of coated electrodes (a basic electrode, B; a high yield rutile electrode, R; a rutile-basic electrode, RB), all having a diameter of 3.25 mm, have been studied with the routine described above. The welding was performed on stainless steel containing 18% chromium and 8% nickel.

Fumes were collected in the laboratory arrangement (AKSELSSON *et al.*, 1977) shown schematically in Fig. 1. The fume is slowly sucked up through the column by the fan. Via a probe, which sweeps over the column section in a spiral path, the fume is sucked isokinetically to the two parallel filters.

For this feasibility test, five samplings were performed per electrode. The ratio between the masses of the loadings of the paired filters A and B was about unity. (The mean of 15 samplings was 1.02 and the standard error of the mean was 0.02.)

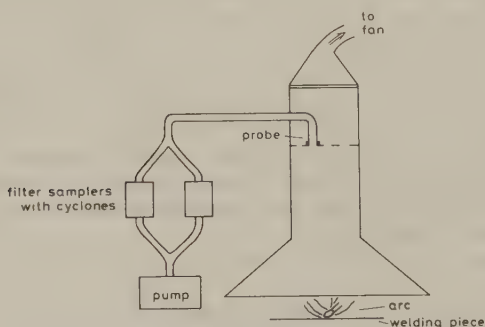


FIG. 1. The sampling arrangement designed by Malmqvist *et al.* (AKSELSSON *et al.*, 1977).

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RESULTS

Table 1 lists the PIXE results for the fumes from the three electrodes. Chromium constitutes 2.5–5% of the total mass and about 70–90% of the chromium is readily soluble.

The analyses of the washing waters with the DPC method show the percentages of soluble Cr(VI) to be 1.7 ± 0.1 , 1.5 ± 0.4 and 3.2 ± 0.3 of the total mass of the samples from electrodes R, RB and B, respectively. The uncertainties given are the limits of the 95% confidence interval.

Figure 2 shows ESCA spectra of an unwashed and a washed sample from the rutile high yield electrode. It is evident that there is Cr(VI) and Cr(III) on the particle surfaces before as well as after washing and that after washing the ratio between Cr(VI) and Cr(total) had decreased. Quantification of the ratios between chromium (VI) and chromium (total) has been estimated after calibration with a set of standards with the ratios 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0, prepared by mixing Cr_2O_3 and $\text{K}_2\text{Cr}_2\text{O}_7$. For the rutile electrode, ESCA data show 55–65% Cr(VI) before washing and 20–30% after washing. For electrodes B and RB, ESCA data show 90–100% Cr(VI) before washing. After washing, the concentrations of Cr(VI) and Cr(III) were too low to be detected by ESCA.

Table 2 summarizes the results. A large fraction of the chromium has been dissolved in the washing process, and in the residues after washing a large fraction is chromium III. Only the rutile electrode contains insoluble chromium VI. In this case, the detection limits prohibit ranking of the electrodes according to their chromium content of the fume. Figure 3(a) shows typical particles as seen in transmission electron microscopy. A low density material, probably derived mainly from the electrode coating, surrounds a high density core material, and acts as a glue holding aggregates of particles together. The shell has a thickness of about $0.03 \mu\text{m}$; the material under it is not available for ESCA for reasons which have already been discussed.

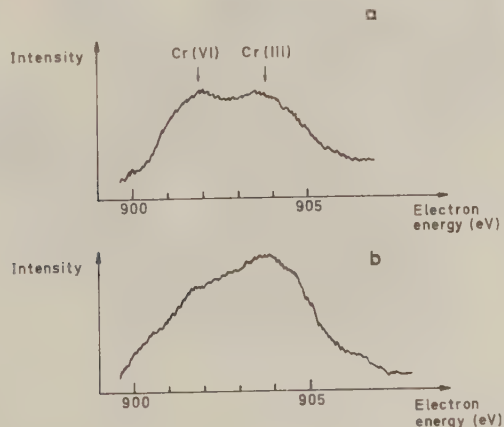


FIG. 2. ESCA spectra of (a) an unwashed and (b) a washed sample from a rutile electrode.

TABLE 1. ELEMENT CONCENTRATIONS IN THE FUME FROM THE THREE DIFFERENT ELECTRODES FOUND BY PIXE ANALYSIS.
THE ACCURACY IS ABOUT 10%, n IS THE NUMBER OF OBSERVATIONS

Element	Concentration in per cent and limits of the 95% confidence interval			
	Electrode R ($n = 5$)		Electrode RB ($n = 5$)	
	unwashed	washed	unwashed	washed
Cl	<0.2	<0.2	0.8 ± 0.4	0.6 ± 0.4
K	21 ± 1	2.8 ± 0.5	23 ± 2	24 ± 5
Ca	1.2 ± 0.1	0.19 ± 0.02	4.5 ± 0.6	0.8 ± 0.3
Ti	2.1 ± 0.2	1.6 ± 0.2	1.5 ± 0.2	1.1 ± 0.5
V	0.05 ± 0.01	<0.02	<0.1	<0.05
Cr	3.4 ± 0.2	0.94 ± 0.12	2.9 ± 0.3	0.7 ± 0.3
Mn	2.7 ± 0.1	1.6 ± 0.2	15 ± 1	12 ± 5
Fe	3.3 ± 0.2	2.6 ± 0.3	2.8 ± 0.3	2.6 ± 0.8
Ni	0.22 ± 0.02	0.17 ± 0.03	0.38 ± 0.04	0.29 ± 0.06
Zn	0.33 ± 0.06	0.18 ± 0.04	0.18 ± 0.05	0.16 ± 0.06
			Electrode B ($n = 5$)	
			unwashed	washed
			0.5 ± 0.2	0.15 ± 0.02
			24 ± 5	0.71 ± 0.07
			12 ± 2	3.1 ± 0.5
			0.6 ± 0.1	0.5 ± 0.1
			<0.05	<0.02
			4.0 ± 0.7	0.34 ± 0.06
			3.0 ± 0.6	2.1 ± 0.3
			4.3 ± 0.8	4.0 ± 0.5
			0.31 ± 0.08	0.28 ± 0.05
			0.25 ± 0.04	0.17 ± 0.03

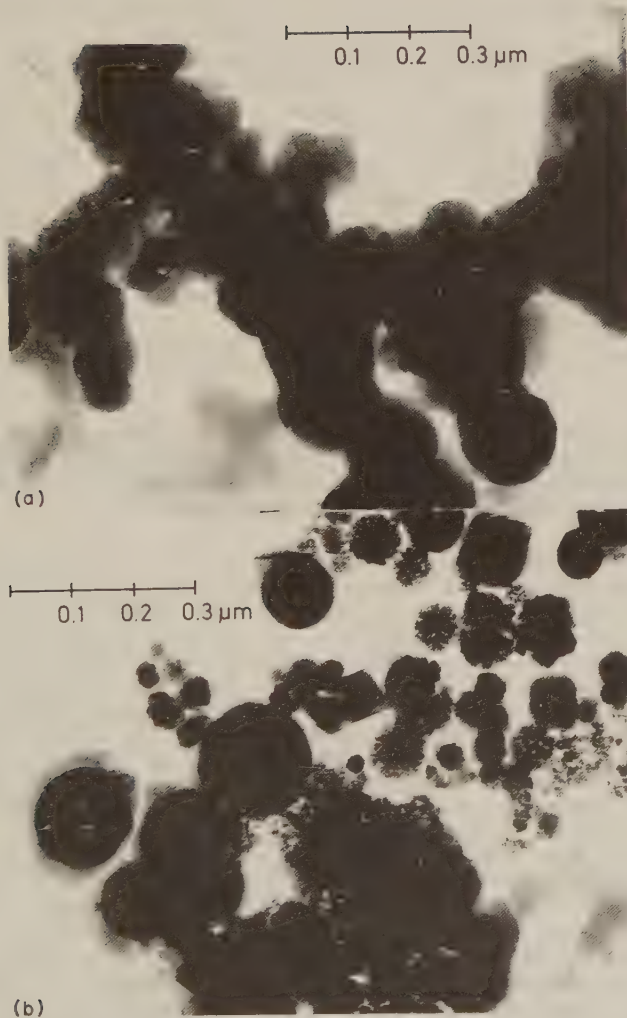


FIG. 3. Welding fume particulates as obtained by transmission electron microscope. Part (a) shows an unwashed sample and part (b) a washed sample. Notice the shell in (a) and the structure of the cores in (b); also the different appearance of the conglomerates in the two figures.

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TABLE 2. SUMMARY OF INFORMATION ABOUT CHROMIUM IN WELDING PARTICLES FOUND IN THIS INVESTIGATION. 'INSOLUBLE' AND 'SOLUBLE' MEAN UNDISSOLVED AND DISSOLVED RESPECTIVELY IN THE WASHING PROCEDURE DESCRIBED IN TEXT

Method	Fraction	Percentage of chromium and limits of the 95% confidence interval		
		electrode R	electrode RB	electrode B
1 PIXE	total Cr	3.4 ± 0.2	2.9 ± 0.3	4.4 ± 0.3
2 PIXE	insol Cr	0.94 ± 0.12	0.67 ± 0.25	0.34 ± 0.06
3 (1)-(2)*	sol Cr	2.5 ± 0.2	2.2 ± 0.4	4.0 ± 0.3
4 DPC	sol Cr(VI)	1.7 ± 0.1	1.5 ± 0.4	3.2 ± 0.3
5 (3)-(4)*	sol Cr(III)	0.71 ± 0.25	0.69 ± 0.53	0.80 ± 0.4
6 ESCA†	insol Cr(VI)	0.25 ± 0.03	<0.2	<0.3‡
7 (2)-(6)†	insol Cr(III)	0.69 ± 0.12	0.67 ± 0.25	<0.3‡

* The difference between the analytical values mentioned.

† Assuming the Cr(VI)/Cr (total) ratios from ESCA to be representative for the samples.

‡ The chromium concentration is too low after washing to be detected by ESCA.

After washing [see Fig. 3(b)], a large part of the low density material is dissolved and information about the core material is obtained. Often the core is found to consist of an aggregate of small round particles of diameter about 0.01 μm . ESCA data are representative of about 80% of the particles of this size.

Associated errors

Some chromium VI may be reduced by the filter material and or by other constituents of the fumes (NIOSH, 1975). Acid environments facilitate the reduction. In ESCA, only the outermost nanometers of the sample are analysed and, because the thickness of the sample is normally of the order of 1 μm , the degree of reduction associated with the filter medium is not significant. To test how the Cr(VI)/Cr (total) ratio depends on the time between sampling and ESCA treatment, samples from electrode R fumes have been analysed 3 h to 5 months after sampling. One of the samples was stored under vacuum for 4 h and exposed to air less than 3 min before analysis. No significant (<10%) change in the chromium ratio due to storage was found, suggesting that reduction between sampling and analysis performed within hours or even days is negligible.

There have been reports of reduction due to heating and/or X-rays from ESCA (DE ANGELIS, 1976). For the fumes from the electrodes B and RB reduction can be neglected; almost 100% has been shown to be Cr(VI) before washing and neither Cr(III) or Cr(VI) were detected by ESCA after washing.

Figure 4 shows how the ESCA results for electrode R depend on the irradiation time. This time is defined as the time between onset of the irradiation and detection of the peak intensity of the Cr(VI) 2p_{3/2} electrons. The reduction effect is clear but not significant for health hazard assessment purposes. However, the ESCA-analyser used is not equipped either with a monochromator for the exciting Al K X-rays or with a modern focusing analyser. By using an ESCA-apparatus including these devices, a much less intense Al K X-ray beam could be used, which would eliminate the reduction effect almost completely.

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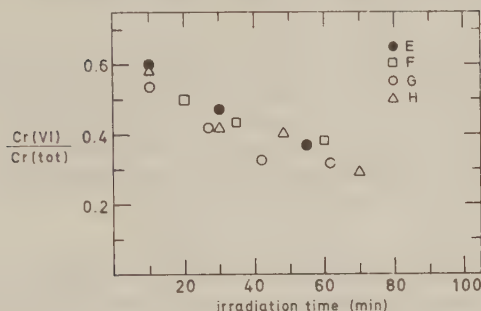


FIG. 4. The ratio Cr(VI)/Cr (total) from ESCA as a function of the irradiation time for particles generated in welding with electrode R. The samples E-H are identical but for sample E 4 h 45 min elapsed between sampling and the start of irradiation, for sample F 3 h 40 min elapsed, for sample G 35 days elapsed and for sample H 35 days elapsed. Sample H was cooled to -50°C during the irradiation whereas samples E-G were cooled to $+25^{\circ}\text{C}$.

In the current work, the uncertainty due to reduction in the prepared standards is less than 10%.

Washing

The use of buffered solutions of pH 7.4 minimizes the risk of reduction or oxidation during washing. This pH value is also presumed to resemble that encountered by particles in the lung. In the washing procedure 25 ml of the buffered water was slowly filtered through the filter giving a washing time of 4–5 min per sample. By repeating the washing procedure in fresh buffered water, no more Cr(VI) could be washed out (less than 0.1% of the mass of the fume). Thus, this procedure separates the readily soluble chromium from the less soluble.

If insoluble chromium passes through the filter during washing in particulate form, other insoluble elements are expected to follow in the same proportions. However, from Table 1 it can be seen that, e.g., 80–100% of the iron stays on the filter. Another test was performed by letting the washing water pass very slowly through a filter of pore diameter $0.4\ \mu\text{m}$. This filter was analysed by PIXE. Virtually no chromium (0.05% of the original chromium in the sample) was found on this filter. For electrode R the washing water was sucked through a filter having a pore diameter of 25 nm, and the chromium caught in this was less than 0.003% of the original chromium. This shows that particles do not pass through the filter in the washing process.

Interferences in colorimetry and ESCA analysis

A multielemental method such as PIXE is very useful in estimating the effects of interference in the colorimetric and ESCA techniques used. The major interfering ions in the DPC method for Cr(VI) analysis are Mo(VI), Hg(II), Fe(III) and V(V) (SANDELL, 1959). The PIXE results shown in Table 1 indicate that molybdenum and mercury are absent (less than 0.2%) in both the washed and unwashed welding samples, but that small amounts of vanadium (about 0.05%) are present in the latter. Interference from these small amounts of vanadium is negligible because good results may

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be obtained provided the ratio of vanadium to chromium (VI) is less than 10:1 (SANDELL, 1959).

In a sulphuric acid solution with chlorine absent, the yellow colour developed by iron is not strong and fairly good results are obtained when the transmittance of the solution is measured above a wavelength of 460 nm (SANDELL, 1959). In this experiment, because the absorbance was measured at 540 nm immediately after the addition of the reagent and because the chlorine concentration was less than 1% according to the results of the PIXE analyses, the interference from iron is assumed to be negligible.

CONCLUSIONS

A procedure is described for the determination of chromium of different solubilities and different oxidation states for monitoring airborne particulates in work environments. The routine is feasible for samples consisting of very small particles. For larger particles, information about surface concentrations can be obtained and the surface concentrations may be most relevant for health hazard assessments. However, for homogeneous particles, extrapolations to bulk concentrations from the ESCA-data may not be reliable. As further information about the absorption mechanisms of chromium in the lungs becomes available, the washing procedure should be appropriately adjusted.

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CHARACTERISTICS OF AEROSOLS CONTAINING CHROMIUM AND NICKEL FROM SOME THERMAL SPRAYING OPERATIONS

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Abstract

Characterizations of aerosols, emitted from five methods of thermal spraying with materials containing chromium and nickel, were carried out. The characterization procedure includes the determinations of the metal content, the particle size distribution, the oxidation state of chromium and a measure of the solubility of chromium. Three different kinds of samplers and the analytical methods PIXE (Particle Induced X-ray Emission analysis), ESCA (Electron Spectroscopy for Chemical Analysis), AAS (Atomic Absorption Spectrophotometry), spectrophotometry with DPC-reagent (sym-diphenylcarbazide) and TEM (Transmission Electron Microscopy) were used. The relative concentrations of the major elements in the aerosols agree with the relative abundances in the spraying material. A considerable part of the aerosol mass was found in the respirable fraction. Mass median aerodynamic diameters in the respirable fractions were below 0.5 μm . Hexavalent chromium, which is the oxidation state of chromium with the highest health hazard potential, was determined. Less soluble hexavalent chromium was detected in some of the spraying methods.

Introduction

Thermal spraying is a technique for coating objects with a surface layer of material with high resistance to e.g. wear and effects of chemical agents (3). The technique is often used for repairing machine details. The material which is to be deposited is heated by either an oxygen-acetylene flame (flame spraying), an electric arc (electric arc spraying) or in a plasma (plasma spraying). The heated material is brought to the object by either the expanded gas (flame spraying and plasma spraying) or by using a jet of compressed air (flame spraying and electric arc spraying). The usage of a large variety of materials with different properties occurs. Metals such as molybdenum, aluminum, copper, zinc, chromium and nickel are often components of the spraying materials, which can be in the form of wires (all methods) or powders (flame and plasma spraying).

The use of this technique give rise to various environmental problems such as high noise levels, UV-radiation and the emission of toxic gases and aerosols.

When carrying out epidemiological research on occupational hazards of exposure to airborne particles containing chromium and nickel, there is a lack of knowledge about the character of the aerosols (11) and hence the objective of this study was to characterize the aerosol emission from methods of thermal spraying with materials containing chromium and nickel. Chromium and nickel are among the most toxic metals used in thermal spraying materials. There is extensive documentation of the toxicity of different chromium and nickel compounds (9,10). Several compounds of these metals have been shown to be carcinogenic. For chromium the oxidation state is of major importance. Cr(VI)-compounds have much higher health hazard potential than Cr(III)-compounds. There is no evidence of carcinogenicity for extra cellular Cr(III)-compounds. For Cr(VI)-compounds water solubility is also a parameter of considerable interest. Indications exist that the less soluble compounds are those of highest carcinogenicity (11).

The toxicity of an aerosol is strongly dependent on the particle size

distribution and the chemical composition of the particles. The characterization procedure used in the present work includes the determination of the particle size distribution, the elemental composition, the oxidation state of chromium and a measure of the solubility of chromium.

Materials and methods

Thermal spraying methods

Five common methods of thermal spraying with materials containing chromium and nickel were chosen. The techniques flame spraying, electric arc spraying and plasma spraying were included. Table 1 describes the methods.

SPRAYING METHOD	SPRAYING MATERIAL	SPRAYING EQUIPMENT	PERCENTAGE OF THE MAJOR METALS IN THE MATERIAL (% of weight)	DIAMETER OF WIRE (mm)	SPRAYING CAPACITY (kg/h)
1a. flame spraying	wire METCOLOY 2	METCO 10E	Fe: 85 Cr: 13 Ni: 0.5	3.17	5.9
1b. flame spraying	wire METCOLOY 2	METCO 3K (3 spraying guns)	Fe: 85 Cr: 13 Ni: 0.5	4.76	3 x 7.26
2. flame spraying	powder METCO 44	METCO 5P	Ni: 76 Cr: 16 Fe: 8	-	8.2
3. flame spraying	wire METCOLCY 33	METCO 10E	Ni: 60 Cr: 16 Fe: 22.5	3.17	5.9
4. electric arc spraying	wire METCOLOY 2	METCO RG (32V, 320A)	Fe: 85 Cr: 13 Ni: 0.5	2.31	14.5
5. plasma spraying	powder METCO 44	METCO 3 MB	Ni: 76 Cr: 16 Fe: 8	-	9.1

Table 1

The spraying methods used. Spraying equipment and spraying materials were manufactured by METCO AB. Settings of gas mixtures, gas flows etc. and distance between the nozzle of the spray-gun and the object according to the recommendations of the manufacturer. Method 1 b was used during sampling under normal production conditions.

Sampling

The spraying and the sampling of aerosols from the five methods were performed in a room sealed off from other activities in a thermal spraying workshop. For one of the methods the characterization was also performed during normal production, where a paper-mill roll was coated with a chromium containing material by flame spraying. A higher spraying capacity, than for the "sealed room" measurements of the same method, was used.

In conventional sampling personal monitors are used. So-called total filter samplers for a "total fraction", or collection on filters after a pre-collection stage for the respirable fraction. Since the main purpose of this study was to explore the emission of aerosols from thermal spraying operations we used more well-defined sampling procedures. For sampling during the normal production, however, personal monitoring was also performed.

The definition of the "total" fraction is often dependent on a specific sampling system and specific sampling conditions. The upper limit of particle size collected depends on the design of the sampling inlet and the air flow rate. Speed and direction of the air movement around the inlet also strongly influence the particle size characteristics of the aerosol collection. Criteria for perfect sampling have been suggested by Agarwal and Liu (2) and Davis (5). The purpose of these criteria is to secure a complete sampling of an aerosol with particles below a given size. For purposes of health effect assessment Vincent and Armbruster (14) suggest sampling procedures with particle size collection efficiencies simulating the collection efficiency of the human respiratory system as determined by experimental studies.

There has been an extensive discussion during the last few years about methods and criteria for fractionating aerosols according to particle size for health effect evaluations. In a recent suggestion for an ISO-standard (12) the total suspended particles are divided into fractions which should reflect probable deposition sites in the human

respiratory system based on the available data from lung deposition studies. An "inspirable" fraction is defined as the part of the total suspended particles which reaches the human airway. The inspirable fraction consists of an extra-thoracic and a thoracic fraction. The thoracic fraction is further divided into two sub-fractions; respirable and tracheo-bronchial. For the respirable fraction there are two definitions; The BMRC-definition (British Medical Research Council) and the ACGIH-definition (American Conference of Governmental Industrial Hygienists). Approved instruments for respirable sampling according to the British and American standards can be used, after a precollection stage according to the definition of the inspirable fraction, for sampling according to the suggested standard. However even if the instruments are used without any precollection stage the differences in collection efficiencies are below the permissible error laid down by the ad hoc working group of ISO (12).

Techniques for "total" sampling and respirable sampling were utilized in the present work. The choice of sampling techniques was determined by the demands on them for well defined particle size fractionations and for generating samples suitable for various analytical techniques. Our intentions were further to collect fractions which could be compared with samples obtained by personal monitoring (total and respirable). However, since personal sampling with "total" samplers does not constitute well defined sampling with respect to particle size, only rough comparisons can be performed. Orientation of the sampler and local air movements around the bearer and the sampler can strongly influence the particle size characteristics of the sampling. The definition of "total" fraction in this work is given in figure 1, which also shows the respirable fraction and the fractions according to the suggested ISO-standard. The "total" sampling was performed for estimation of the relative fraction of the respirable fraction in conventional total filter measurements (idealized case) and for estimation of the relative abundances of elements in different size fractions. Care should however be taken when drawing conclusions about the health hazard potential from information on the magnitude of the coarse fraction. The relevance of sampling different particle size fractions to what actually is inhaled by humans in different situations was recently discussed by Vincent and Mark (16).

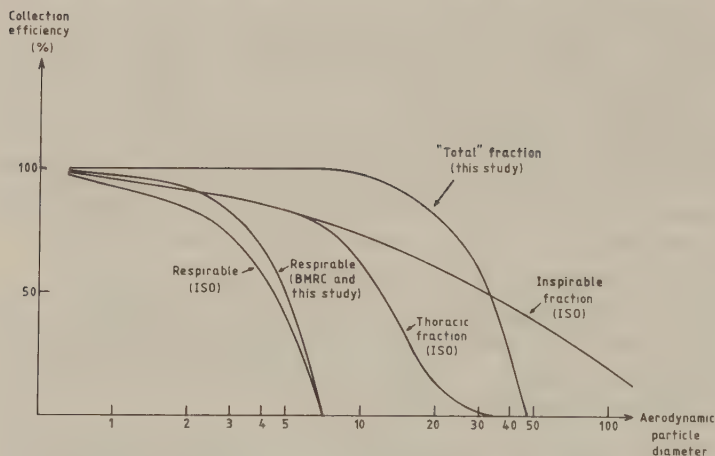


Figure 1. Theoretical collection efficiencies for the multi-filter sampler as a function of aerodynamic particle diameter. For comparison the suggested ISO-standard for thoracic fraction and inspirable fraction are given. The respirable fraction used is that of the BMRC standard for respirable dust.

Three types of samplers were used: 1) a multi-filter sampler for total and respirable fractions, 2) a modified Battelle impactor and 3) a sampler with two parallel filters prepared for transmission electron microscopy studies.

Figure 2 shows the multi-filter sampler. It consists of four filters (Millipore GSWP, 37 mm diameter, $0.22\text{ }\mu\text{m}$ pore size), two of them with pre-collectors (cyclone pre-collector; Casella Personal Sampler) (A and B) and two without (C and D). A cylindrical common inlet with a length of 300 mm and a diameter of 50 mm was used to avoid the effects of turbulence which would affect the collection efficiency. The inner surface was of aluminum, electrically ground, in order to minimize losses due to electrostatic effects. The air flow through each filter was 1.9 l/min which is the nominal flow of the pre-collectors used.

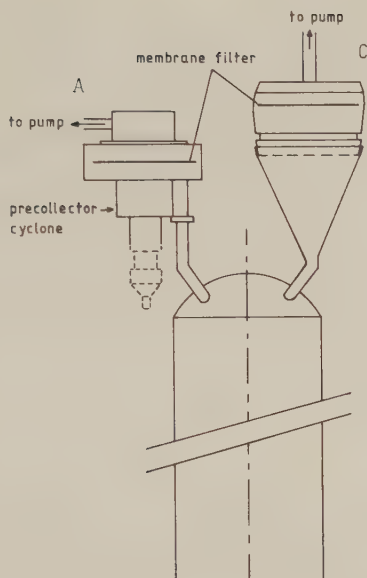


Figure 2. The multi-filter sampler. The figure shows two (A and C) of the four (A,B,C and D) filter holders. They are symmetrically connected to the top of the sampling tube. The air flow through each filter is 1.9 l/min. The filters after the pre-collector cyclones (A and B) collect particles according to the Johannesburg convention (BMRC-curve).

The sampler was intended to give samples for a) gravimetical determination of the ratio between respirable and total fraction, b) analysis of the elemental composition of particles in the two fractions and c) determination of the oxidation state of chromium. The multi-filter sampler was designed for sampling a large fraction of the total aerosol. The upper limit of particle size depends mainly on the sedimentation rate in the inlet tube. Figure 1 shows the theoretical inlet characteristics for sampling in calm air. The mean of the M_A/M_B and M_C/M_D -ratios, where M_A , M_B , M_C and M_D denote the gravimetrically determined mass of particles collected on the filters, were 1.04 ± 0.10 and 0.97 ± 0.14 respectively for 25 collections (the uncertainties are given as one standard deviation of the distribution).

The modified Battelle impactor (8) was used for obtaining a more differentiated determination of the particle size distribution within the respirable fraction. The impactor consists of six impaction stages and one filtration stage. The collection substrate of each impaction stage is a glass plate with a thin ($\sim 30 \mu\text{g}/\text{cm}^2$) polystyrene foil. The foil is coated with a thin layer of paraffine to obtain a sticky surface for reducing bounce-off and re-entrainment effects. The impactor divides the particles into seven particle size fractions with the aerodynamic cut-off diameters 8, 4, 2, 1, 0.5 and $0.25 \mu\text{m}$ respectively (stages 1, 2, 3, 4, 5, 6 and a filter collecting particles with diameters below $0.25 \mu\text{m}$). The impactor was modified by giving an excentric rotation to the collection plates of stages 4 and 5 as described in a personal communication by K.G. Malmqvist, Lund Institute of Technology. Using this modification a thin deposite of particles is achieved, thus minimizing collection losses. The substrates of stages 4 and 5 were the most heavily loaded for all spraying methods used. After sampling the polystyrene foils are floated off the glass plates onto water and collected on aluminum frames for subsequent irradiation with protons in the PIXE -analysis (7). As the impactor in this study was intended for fractionation of the respirable particles, the inlet collection characteristics for coarse particles were not taken into consideration. The first stage, collecting particles larger than $8 \mu\text{m}$ aerodynamic diameter, was used as a pre-collector stage removing coarse particles.

For studying individual particles with transmission electron microscopy, a double filter sampler was used for particle collection. Before sampling the filters are coated with a carbon layer by evaporation. Before examination the filters are again coated with a carbon layer and the filter matrix dissolved in ethylacetate, thus achieving a thin sandwich of carbon with particles in between, suitable for transmission electron microscopy studies.

The samplers were placed 50 to 150 cm above and 50 to 100 cm behind the spraying object with the inlets facing downwards during sampling. The distance between the nozzle of the spray-gun and the object were between 5 and 20 cm. Five collections with each sampler were performed for each spraying method.

The same characterization procedure was also applied to one of the methods during normal production. The samplers used for characterization were placed at different places in the spraying hall. Personal monitoring equipment was carried by two of the operators during spraying. "Millipore monitors" with Millipore filters (Millipore AAWP, 37 mm diameter, 0.8 μ m pore size) were carried for two working days during continuous spraying. The filters were changed every other hour. There were other activities in the hall during the personal sampling, however none of them emitting chromium-containing aerosols. The personal sampling was complemented with a stationary "Millipore monitor".

Analytical methods

To gain maximum information from the samples several analytical methods were used. Gravimetrical analysis was applied to the filters from the multi-filter sampler by using a Sartorius balance with 1 μ g precision and accuracy. Particle Induced X-ray Analysis (PIXE) was used for elemental analysis at the Lund PIXE facility (7). This method gives fast and reliable results for elements heavier than phosphorus. The detection limits are typically below 1 ng. One of the respirable and one of the total samples (B and D) from the multi-filter sampler were washed in distilled water buffered to pH 7.4. A procedure for analysis of chromium described by Bohgard et al. (4) including PIXE, ESCA (13) and spectrophotometry with DPC reagent (1) was used. In the present study AAS, with Perkin-Elmer 403, was used as a complement to the procedure for determining the total fraction of soluble chromium. The sample treatment is described in figure 3. Knowledge about the structure of individual particles is essential for evaluating the results from ESCA, since the results from ESCA are valid only for a thin surface layer (~2 nm) of the sample. Transmission electron microscopy was used to study individual particles before and after washing. It should be noted that "solubility" in this study is defined as the relative amount which is leached out by washing a filter with 25 ml distilled water (at 37°C) buffered to pH 7.4 according to the procedure described by Bohgard et al. (4).

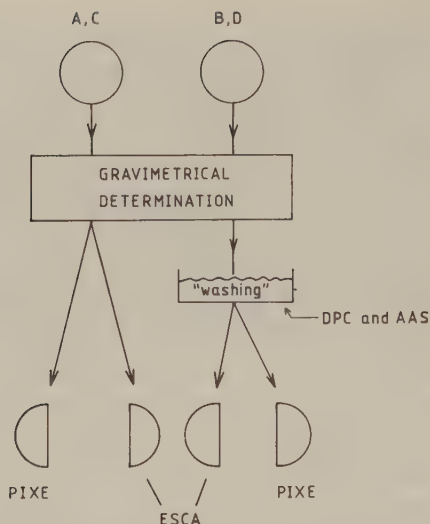


Figure 3. Sample preparation and analytical methods applied to the filters from the multi-filter sampler. A and B are filters with the respirable fraction. C and D are the filters for the "total" aerosol measurements.

Results and discussion

Elemental composition

Table 2 shows the results from the analyses of the filters from the multi-filter sampler. The relative abundancies of the major metals in the aerosols agree with the relative abundancies in the spraying materials. The lower concentrations of the metals in the fume relative to the materials can be explained by the fact that the fumes consist of metal oxides while the spraying materials consist of alloys of the metals. Previous studies of welding aerosols (6) have shown considerable enrichment of certain elements in the fume from the consumable. However, in the present study no such effects were observed for the major elements in thermal spraying operations. The differences in metal concentrations between the total and the

respirable fraction are below 10%. Other elements than those given in table 2 were detected, but due to their low concentrations (<1%), there is a risk that other activities in the workshop may have influenced the results. When the same spraying material was used for different methods (flame spraying and electrical arc spraying with METCOLOY 2, flame spraying and plasma spraying with METCO 44) minor differences in metal composition were seen.

Figure 4 shows the results from the measurements with the personal monitors carried by two workers during the spraying of a paper mill roll. The ratio between chromium and iron concentration is not significantly different from the ratio obtained from the characterization procedure (table 2).

		METHOD					
		1a flame spraying METCOLOY 2	1b flame spraying METCOLOY 2	2 flame spraying METCO 44	3 flame spraying METCOLOY 33	4 electric arc spraying METCOLOY 2	5 plasma spraying METCO 44
METAL % of aerosol mass (total and respirable fraction)	Cr	5.6 ± 0.2	7.3 ± 1	9.4 ± 0.3	7.3 ± 1.7	7.3 ± 0.7	8.2 ± 0.8
	Fe	40 ± 2	44 ± 4	2.8 ± 0.1	6.6 ± 1	41 ± 4	3.2 ± 0.5
	Ni	< 1	< 1	35 ± 2	22.5 ± 3	< 1	30 ± 3
respirable mass/total mass (%)		45 ± 2	39 ± 3	92 ± 1	50 ± 4	83 ± 2	54 ± 2
Cr- fractions in total aerosol	percentage soluble Cr of Cr	7.7 ± 1	3.6 ± 1	3.2 ± 1	13 ± 1	6.4 ± 1	10 ± 1
	percentage soluble Cr(VI) of Cr	6.6 ± 1	3.1 ± 1	1.9 ± 1	10 ± 1	5.1 ± 2	9.7 ± 1
	percentage Cr(VI) of Cr on sample surface	51 ± 5	50 ± 5	< 20	70 ± 5	22 ± 5	63 ± 5
	percentage Cr(VI) of Cr on sample surface after washing	< 15	27 ± 5	< 15	18 ± 5	18 ± 5	20 ± 5
Cr- fractions i res- pirable part of aerosol	percentage soluble Cr of Cr	21 ± 4	6.2 ± 3	2.1 ± 0.2	26 ± 3	9 ± 2	23 ± 2
	percentage soluble Cr(VI) of Cr	18 ± 5	5.8 ± 0.5	1.8 ± 0.2	25 ± 4	9 ± 2	22 ± 2
	percentage Cr(VI) of Cr on sample surface	50 ± 5	52 ± 5	< 20	73 ± 5	22 ± 5	69 ± 5
	percentage Cr(VI) of Cr on sample surface after washing	< 15	22 ± 5	< 15	< 15	17 ± 5	36 ± 5

Table 2

Results from analysis of filters from the multi-filter sampler. Concentrations of metals in the fume, percentage in the respirable fraction and percentage of different fractions of chromium in the total and respirable fraction are given. The uncertainties are given as one standard deviation of the mean from the analysis of five samples.

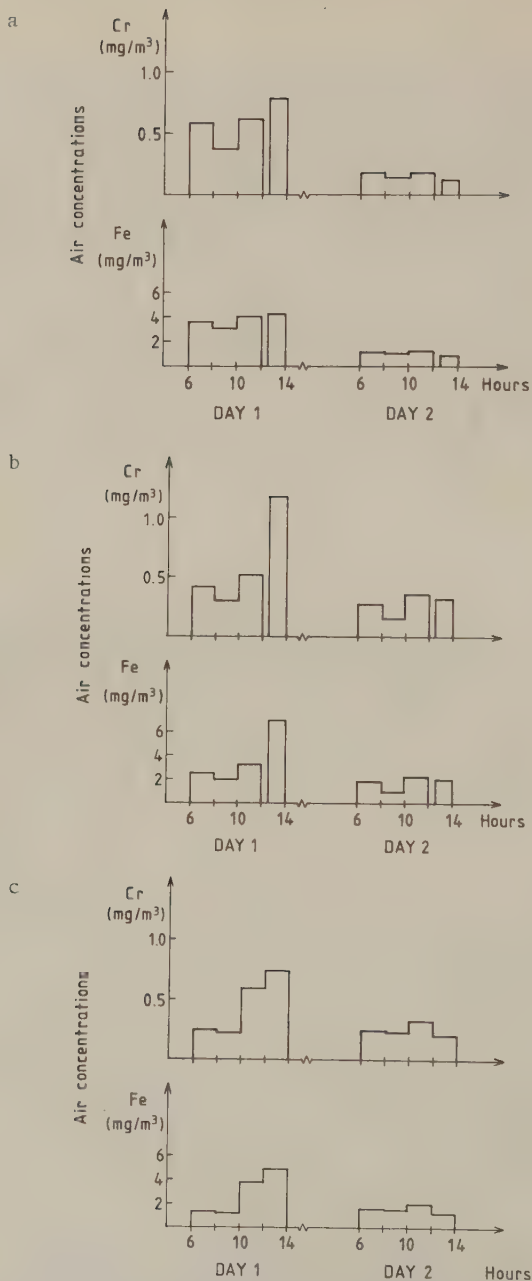


Figure 4. Exposures for chromium and iron obtained from personal sampling (a and b) during two days for two thermal spraying operators coating a paper mill roll by flame spraying with METCOLOY 2. Figure 4c shows the results from a stationary Millipore monitor.

Particle size distribution

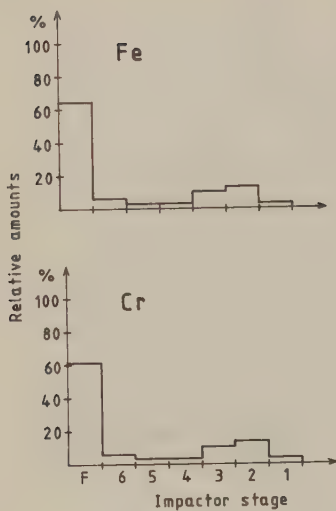
The ratios between the masses of respirable and total fractions are given in table 2. The methods flame spraying with powder and electrical arc spraying give higher percentages in the respirable fraction than the other methods. Figure 5 shows the particle size distributions for fine particles. Significant differences between the methods occur, but for all the five methods the finest particles dominate the mass of the respirable fraction. For method 2 (flame spraying with powder) the mass median aerodynamic diameter of the total aerosol is below $0.5\text{ }\mu\text{m}$. For the other methods the mass median aerodynamic diameters of the respirable fractions are below $0.25\text{ }\mu\text{m}$.

There are no significant differences ($<5\%$) in metal composition between different particle size fractions. Hence, the metal composition of the collected aerosol is independent of the size characteristics of the sampling inlets.

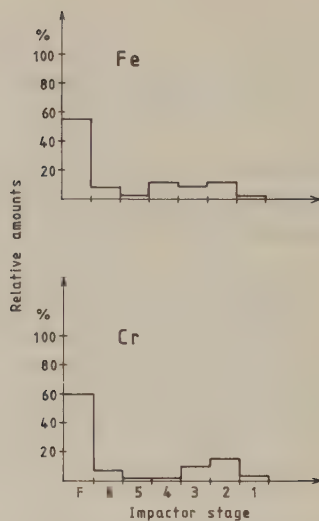
Oxidation state of chromium

Results from the determination of the oxidation state of chromium are given in table 2. There are significant differences in the Cr(VI)-concentration in the respirable and the total fractions. The concentration of Cr(VI) seems to depend on both spraying method and spraying material. The analyses of the soluble part of Cr(VI) were performed within four hours after washing the filters. There is, however, a risk of loss due to the reduction of Cr(VI) to Cr(III). The systematically higher values obtained from the AAS analysis (percentage soluble Cr in table 2) relative to the DPC analysis (percentage soluble Cr(VI) in table 2) may not be significant because of the reduction of Cr(VI) to Cr(III) by other constituents of the aerosol acting as reduction agents during the washing procedure, and the time elapse between washing and analysis. Hence the soluble fraction of chromium may consist entirely of Cr(VI).

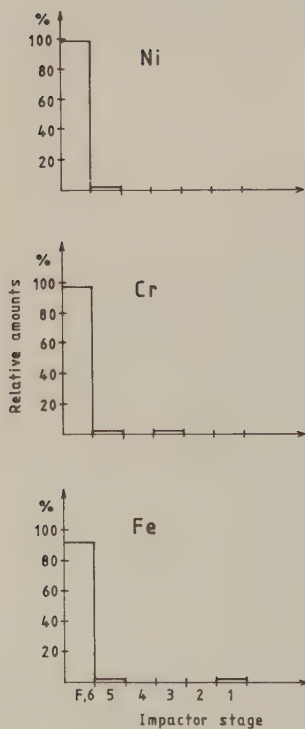
a



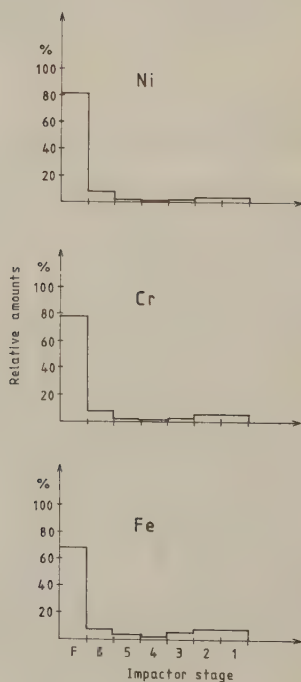
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c



d



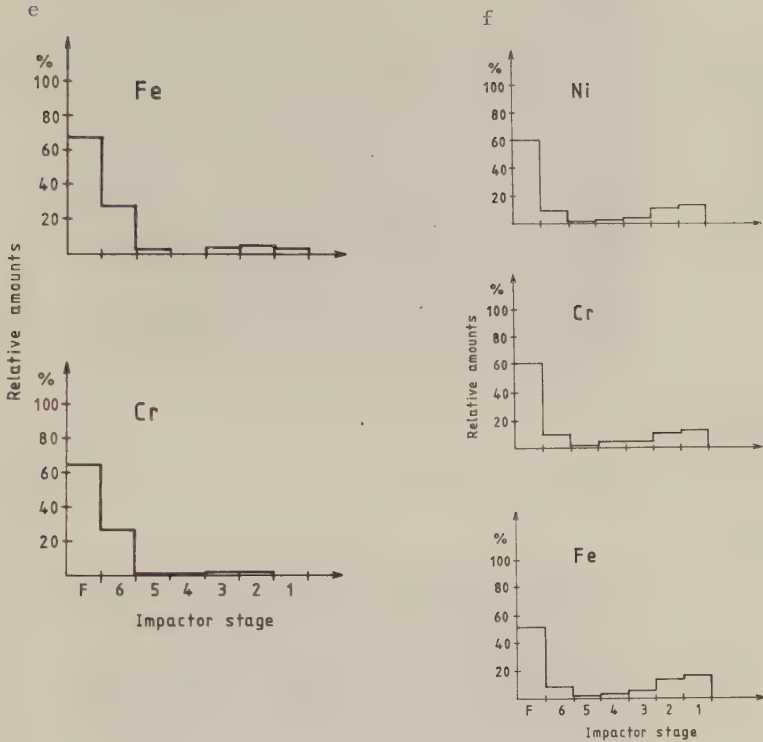


Figure 5. Particle size distributions from impactor measurements. The figures 5a and b show the PIXE-results for chromium and iron from flame spraying with METCOLOY 2 measured in the "sealed room" and during normal production respectively (Methods 1a and 1b). The figures 5 c,d,e and f show results from flame spraying with METCO 44, flame spraying with METCOLOY 33, electric arc spraying with METCOLOY 2 and plasma spraying with METCO 44 respectively. Stage 1 was used as a pre-collector stage collecting particles with aerodynamic diameter larger than $8\text{ }\mu\text{m}$. On the stages 2, 3, 4, 5, 6 and the filter (F) are the fractions with aerodynamic diameters D ; $4 < D < 8$, $2 < D < 4$, $1 < D < 2$, $0.5 < D < 1$, $0.25 < D < 0.5$ and $D < 0.25\text{ }\mu\text{m}$ respectively.

The differences between the concentrations of Cr(VI) in the total and respirable part of the aerosols and the determined mass ratios between respirable and total fractions, indicate that the soluble part of Cr(VI) is mainly in the respirable fraction for all methods. The ESCA-results from unwashed samples do not show significant differences between the total and the respirable fraction. Assuming spherical particles, the total particle area of the respirable fraction exceeds 99% of the total aerosol area according to the determined particle size distributions. Hence by using ESCA, for the spraying methods studied, the respirable fraction dominates the particle area and hence the material analyzed by ESCA. After washing Cr(VI) was still detected for four of the spraying methods. The difference between flame spraying with METCOLOY 2 sampled in the "sealed room" and during normal production conditions should be noted and may be due to the fact that different spraying equipment was used on the two occasions.

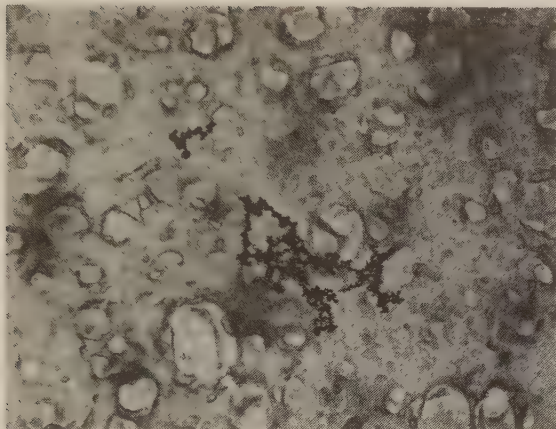
The analytical results of the Cr(VI)-determinations are not unambiguous. There are at least two alternative interpretations of the results; a) Cr(VI) exists only in a surface layer of the particles and is entirely or partly dissolved by the washing procedure. However, our electron microscopy studies do not support the existence of a surface layer with a different composition from that of the bulk material. b) Cr (VI) is homogeneously distributed in the particles. After the washing procedure the surface layer consists of insoluble Cr(III)- and other insoluble metal compounds preventing underlying Cr(VI) from being revealed by washing or by ESCA.

With the current knowledge of the toxicity of Cr(VI)- exposure it is not possible to judge whether the two alternative interpretations are significantly different in terms of health hazard.

Particle structure

Individual particles have been studied with transmission electron microscopy. Figure 6 shows two micrographs with particles typically seen in these studies. Generally two classes of particles can be seen; coarser spherical particles and finer particles being aggregates of

a)

 $1\mu\text{m}$

b)

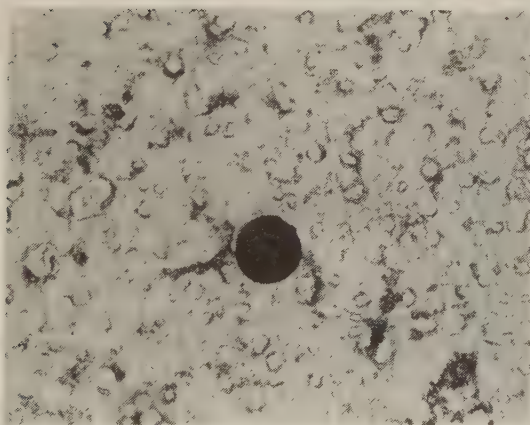
 $1\mu\text{m}$

Figure 6. Transmission electron micrographs of particles from flame spraying with METCO 44; a) an aggregate of primary particles b) a spherical particle.

small ($0.005 - 0.05 \mu\text{m}$) primary particles. The aggregates always dominate over the spherical particles in the micrographs. ESCA is valid for 20 to 80% of the volume of the particles in figure 6 a. The observations further support the assumption made above that the total particle area of the respirable fraction exceeds 99% of the total aerosol area.

Conclusions

The relative elemental compositions of the aerosols for the major elements agree with the relative abundances in the spraying materials used and are independent of particle size. Hence for a collected aerosol, the elemental composition is independent of inlet particle size characteristics of the sampler.

Two modes of particles categorized according to aerodynamic diameter can be seen. The respirable fraction consists of 40-90% of the particle mass in the total fraction as defined in this study. The mass median aerodynamic diameter was below $0.5 \mu\text{m}$ for the respirable fraction, which means that diffusion is the main deposition mechanism of these particles. The particle area in the respirable fraction constitutes more than 99% of the total particle area. A large part of the chromium in a surface layer was found to be hexavalent for four of the methods. Both soluble and less soluble hexavalent chromium were detected. The oxidation state of chromium seems to depend on both spraying method and spraying material.

When the aerosol emission was characterized during normal production, it was found that the aerosol was not significantly different with respect to metal content and particle size distribution.

In thermal spraying, workers may be exposed to high concentrations of aerosols emitted from the spraying process. When using materials containing chromium and nickel, compounds of those metals can constitute the major part of the aerosol. A considerable part of the chromium can be hexavalent. The results imply that a high degree of

precaution has to be taken when working with these processes.

The characterization procedure used in this study has been shown to give detailed data about the aerosol emission from methods of thermal spraying. The knowledge of how the health hazard potential depends on the aerosol characteristics as determined in this work is not sufficient for ranking the five methods studied from a hygienic point of view. However the sampling and analytical techniques used give results of high significance for parameters of considerable interest in health effect assessments and for toxicological and epidemiological studies.

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PERSONAL AEROSOL SAMPLER WITH SIZE FRACTIONATION AND TIME RESOLUTION

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ABSTRACT

This chapter describes a personal aerosol sampler with size fractionation and time resolution that gives samples for elemental analysis. An impaction stage collects coarse particles and a filtration stage collects finer ones. Sampling in consecutive time intervals is performed on different impaction and filtration surfaces. These sampling surfaces corresponding, for example, to 15-min intervals, may be analyzed with particle-induced X-ray emission analysis (PIXE) for fast, low-cost determination of most of the elements of hygienic interest that are present in aerosols in concentrations far below their current threshold limit values (TLV). The sampler is intended to be used for aerosol measurements in work environments to obtain detailed information on exposures.

INTRODUCTION

A personal sampler giving both size- and time-fractionated samples for multielemental analysis would be a useful tool for monitoring exposures to

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airborne particles. In epidemiological and toxicological studies, it is advantageous to have access to many detailed exposure data. When developing elimination techniques and safer working procedures, size- and time-fractionated sampling is useful in evaluating the results of the efforts made during the development work. When the purpose is to monitor elemental compositions and concentrations of air pollutants for comparison with current TLV, samplings over long periods, with subsequent selection of samples for low-cost elemental analysis, can be performed.

During the last decade, PIXE, a method for elemental analysis, has been developed and used at the Lund Institute of Technology. PIXE determines small amounts ($<10^{-9}$ g) of elements in small samples ($\sim 10^{-6}$ g) [Åkesson and Johansson 1979; Johansson et al. 1970]. The samples are irradiated with charged heavy particles, e.g., protons, and the characteristic X-rays emitted are detected in a semiconductor detector. This makes it possible to analyze simultaneously all elements heavier than phosphorus. The method has been used in comprehensive studies of work environment aerosols [Bohgard et al. 1981; Malmqvist et al. 1981]. The capability of the method to allow fast determination of small amounts of elements in small samples has led us to develop a personal aerosol sampler for two particle-size fractions giving time-resolved samples with short sampling intervals, e.g., 15 min.

SAMPLER

Figure 1 shows the principal design features of the sampler. It includes two sampling stages, an impaction stage (collecting coarse particles) and a filtration stage (collecting finer ones). The samples are collected along the edges of two circular aerosol filters mounted on plastic disks. After a preset sampling interval, which can be chosen in steps from 5 min to 2 hr, the two membranes rotate around their common axis through a fixed angle, and collection recommences on fresh impaction and filtration surfaces. The current versions permit a total of 18 sampling intervals.

To rotate the wheels on which the filter disks are mounted, a small electric motor and a gear device are included in the sampler box. The motor is controlled by a simple electronic circuit. To permit precise positioning of the sampling surfaces, one of the wheels is provided with small holes (1-mm diameter) on its outer edge. When one of these holes is positioned so that it allows the light from a light-emitting diode (LED) to reach a phototransistor connected to the control electronics, the motor is stopped. After a pre-selected time interval, the motor starts again and the disks rotate until the next hole is in position.

The weights of the current units vary from 300 to 500 g. Figure 2 shows the design of one of the prototypes. The flowrate for the prototype shown is 0.35 liter/min, maintained by a pump, which, together with batteries and control electronics, is carried on a belt on the person bearing the sampler.

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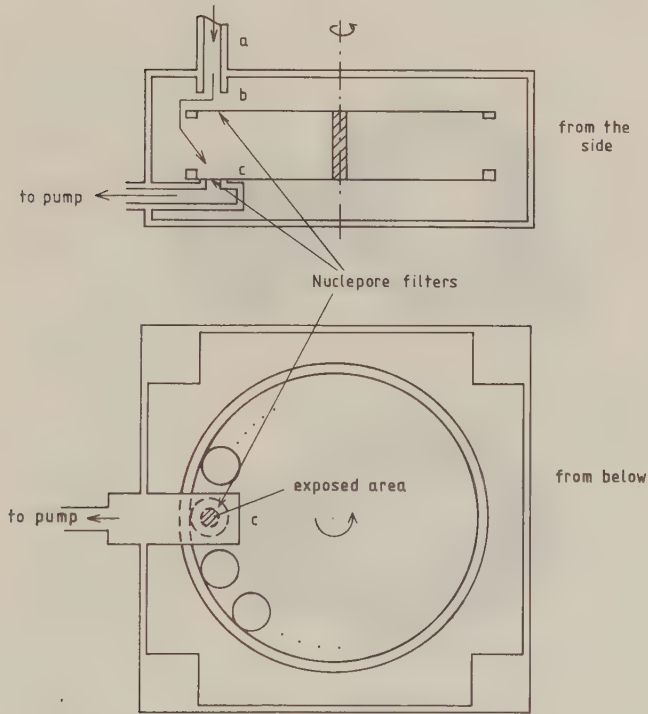


Figure 1. Principles of the personal aerosol sampler. Air is sucked through inlet a and passes an impaction stage b where coarse particles are deposited on a Nuclepore filter coated with Apiezon grease. Fine particles continue to the filtration stage c, where they are deposited on a 0.4- μm Nuclepore filter. The sampler may conveniently be carried near the breathing zone.

FILTRATION STAGE

The choice of filter material is determined by the specific demands placed on it by the sampling and the subsequent PIXE analysis. During the sampling a circular orifice with 3- to 4-mm diameter is sucked to the filter. The filter must have high mechanical strength and a smooth surface if the sampler is to perform properly. In addition, in view of the fact that only a moderate pressure drop across the filter can be obtained using a small pump, the flow-rate through the small filtration area ($\sim 10 \text{ mm}^2$) should be high enough to

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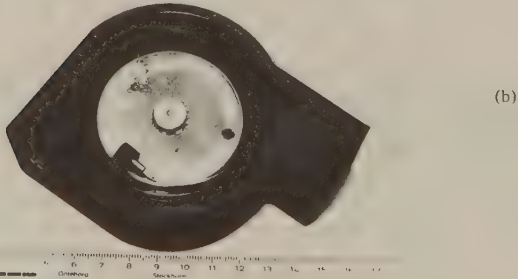
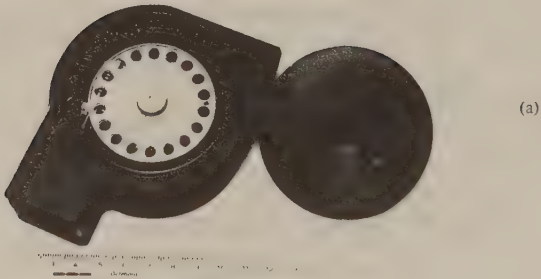


Figure 2. Views showing the design of one of the prototypes: (a) impactation stage; (b) filtration stage; and (c) example of how the sampler may be carried.

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produce samples in which the masses of elements corresponding to air concentrations well below their respective TLV can be detected.

Routine PIXE analyses in Lund are performed by irradiating the filter, including any deposited particles, with 2.55-MeV protons. To get a low background of X-ray radiation and thus achieve low detection limits, the filter should be thin. Furthermore, the filter should contain the lowest possible concentrations of impurities. Certain elements, such as fluorine, must not be present in high concentrations in the filter material since they produce high intensities of γ -rays when irradiated by protons, thus disturbing X-ray detection. Teflon[®] filters, which otherwise have a number of advantages, could not be used due to their high fluorine content, if the samples are subsequently to be analyzed by proton-induced X-ray emission.

Among the available aerosol filters that fulfill most of these demands are the polycarbonate filters manufactured by Nuclepore Corporation. The pore size of the filters is chosen to obtain as high a flowrate as possible while still maintaining high collection efficiency for fine particles. The dependence of filtration efficiency on particle size for typical pressure drops across the type of filter used in the sampler has been measured using a technique similar to that developed by Liu and Lee [1976].

Submicron CuSO_4 aerosols were generated by using a collision atomizer (TSI 3075) and CuSO_4 solutions in concentrations between 0.001 and 0.05 g/ml. An electrostatic classifier (TSI 3071) was used for producing monodisperse aerosols with various particle sizes. To eliminate the net charge of the aerosol, the monodisperse particles were passed through a neutralizer that included a ^{85}Kr β -emitting source. The particles were detected using an electrical aerosol analyzer (TSI 3030) as aerosol detector. Figure 3 shows experimental data on the filtration efficiency as a function of particle size for a Nuclepore filter with 0.4- μm pore diameter. Particle size is defined according to the electrical mobility of the particles. The pressure drop (150 mm Hg) is approximately that of the filtration stages of the personal sampler. The minimum efficiency, 89%, occurs for particles with diameters of 0.05 μm .

The drop in filter efficiency seen in Figure 3 may be explained by regarding the dominating filtration mechanisms [Spurny and Gentry 1979]. Small particles are collected with high efficiency due to the high diffusion coefficient and large particles due to impaction and interception. The minimum occurs for some intermediate particle sizes.

Filter efficiencies for 0.4- μm Nuclepore filters have previously been measured by Liu and Kuhlmei [1977]. They used dioctyl phthalate (DOP) particles and determined the filter efficiency dependence on particle size. Liu and Kuhlmei have measured collection efficiencies at pressure drops of 30 and 100 mm Hg and have got minimum efficiencies of about 94 and 87% at the particle diameters 0.085 and 0.07 μm , respectively. The filtration theories

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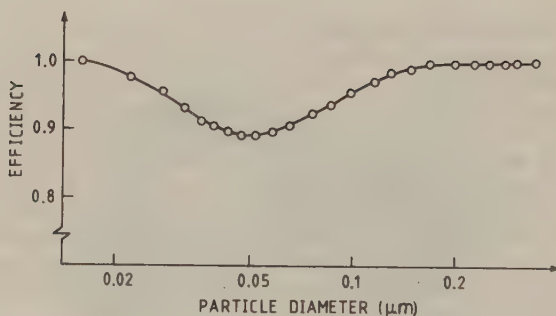


Figure 3. The collection efficiency of 0.4- μ m Nuclepore filters as a function of particle diameter for a pressure drop of 150 mm Hg across the filter.

predict that the collection efficiency due to diffusion decreases while the efficiency due to impaction increases with increasing pressure drop. Hence, a minimum at smaller particle sizes is obtained by increasing the pressure drop. Our results appear to be qualitatively in agreement with those of Liu and Kuhlmeier.

The efficiency obtained using a clean 0.4- μ m Nuclepore filter is sufficient for collecting aerosols with subsequent determinations of element concentration in hygienic assessments. When the filter becomes loaded the efficiency can increase due to clogging [Fan and Gentry 1978]. The maximum flowrate through the sampler at a pressure drop of 150 mm Hg exceeds 0.4 liter/min. The pressure drop is set slightly lower at the beginning of the sampling, giving a flowrate of 0.35 liter/min, allowing for an increase of the pressure drop by a regulated pump at the end of the sampling interval. This is necessary to compensate for increased flow resistance through the filter due to clogging, which may occur.

IMPACTION STAGE

Respirable particles were defined at the Johannesburg Conference [Orenstein 1960]. To collect samples in good accordance with this definition of respirable dust, commercially available minicyclones (e.g., General Purpose Personal Sampler, C. F. Casella & Co. Ltd, London) followed by a membrane filter are used. However, to obtain time resolution for the large particle

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fraction, an impaction stage was chosen in the personal sampler described here.

When experimentally determining the collection efficiency of an impaction stage as a function of aerodynamic particle diameter, a sharp increase in collection efficiency for increasing particle diameter up to approximately 100% is seen at the 50% cutoff diameter. For much larger particles, however, a decrease in efficiency is sometimes noticed due to particle bounce off and reentrainment. To avoid this and any possible effect caused in the fine particle stage if large particles should reach it, the sampler inlet must be designed for sampling particles below a selected maximum diameter, e.g., 15 μm .

In the sampler described, the flowrate will be limited primarily by the filter and the battery-operated pump used. The example given here is for a flowrate of 0.35 liter/min. The impaction stage is then designed for a 50% cutoff aerodynamic diameter of 5 μm . The calculations on which the design was based are taken from Marple and Willeke [1976]. The S/W ratio was chosen to be 1.5 (S = jet-to-plate distance and W = jet width) since Stokes number will in this case be rather insensitive to the small variations in S, which may occur during the rotation of the filter disk. To get the 5- μm cutoff diameter, a circular nozzle of 1.75 mm diameter was chosen, the Reynolds number (Re) being about 300. This rather low Re value yields a not very steep cutoff characteristic as a function of particle size. This is favorable in comparison with the requirements imposed by the Johannesburg convention. It should be pointed out that the 50% cutoff diameter can easily be changed in the interval 1–10 μm by choosing nozzles of different sizes for other cross-sectional areas of the jet.

For proper collection by impaction, it is necessary to suppress bounce off and reentrainment of particles, e.g., by coating the collection substrate with a soft sticky material [Rao and Whitby 1977]. The Nuclepore filters used for the filtration stage can be purchased with a sticky coating of Apiezon vacuum grease; since this type of filter has several favorable properties as a backing for subsequent PIXE analysis, it has also been chosen for the impaction stage. The analytical procedure is simplified and standardized by using the same material, giving the same detection limits for both particle fractions. The use of a filter material as collection substrate in commercial impactors is quite common and, when the airstream partly penetrates the filter matrix, has introduced some errors due to the collection of fine particles by diffusion mechanisms. The well-defined holes in a Nuclepore filter, all nearly perpendicular to the surface, do not permit any such penetration and the filter acts similarly as a plastic foil.

So far the design of the impaction stage is based only on theoretical calculations, but experimental tests by using monodisperse aerosols are currently being made.

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ELEMENTAL ANALYSIS WITH PIXE

In routine PIXE analysis in Lund, the elemental compositions of samples are determined with an accuracy and precision better than 5% [Johansson et al. 1981]. We use a computer program [Kaufmann et al. 1977] that fits a function for both the continuous X-ray background and the characteristic peaks in the X-ray spectra obtained. The intensities of individual characteristic lines can be determined reliably from complex spectra, despite substantial variations in analysis parameters such as beam area and type of X-ray absorber.

For elemental analysis of the time- and size-fractionated samples from the personal sampler, the analyzing parameters are fixed and the irradiation time is kept short (~ 10 sec), thus obtaining low-cost analysis with high capacity both in the analyzing system and the subsequent data evaluation program. At present, samples are irradiated by 2.55-MeV protons for 10 sec. The proton current density is 200 nA/cm^2 . The cross-sectional diameter of the beam is 4–5 mm, thus getting the entire sample area of the filtration stage within the beam area. An X-ray detector [Kevex 80-mm^2 Si(Li)] collimated to an effective area of 30 mm^2 is used to detect the X-rays. An X-ray absorber consisting of a $340\text{-}\mu\text{m}$ -thick Mylar foil with a hole for transmitting 1.7% of the X-ray intensity with low attenuation is positioned between the sample and the detector.

For sampling periods longer than five minutes, the analytical parameters used permit quantification of most elements of hygienic interest with concentrations far below their TLV. Table I shows the current detection limits for a number of elements. The corresponding air concentrations for sampling at 0.35 liter/min in 15-min intervals are also given. The relatively high detection limit for some elements (e.g., cadmium) can be decreased significantly by using longer irradiation times or increased proton energy. It should be pointed out that the values for the detection limits are valid for filters with very low loadings. For heavily loaded filters the detection limits may increase, mainly due to interference between X-ray lines from different elements, especially if one or a few elements drastically dominate the element composition of the aerosol. However, in most cases, the sensitivity is sufficient to detect elements of hygienic interest in small samples (air volumes ~ 5 liters) at levels far below their current TLV.

SIMPLE TEST OF PERFORMANCE

To test the performance of the personal sampler, it has been used for measurements in the breathing zone of a welder, who welded on mild and

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Table I. Detection Limits for a Number of Elements in Fractionated Samples^a

Element	Detection Limits	
	On Filter for 10-sec Irradiation Time (ng)	Corresponding Air Concentration ^b ($\mu\text{g}/\text{m}^3$)
S	68	13
Cl	56	11
K	32	6
Ca	18	3
Ti	7	1
V	5	1
Cr	8	2
Mn	3	0.5
Fe	2	0.3
Co	2	0.3
Ni	2	0.4
Cu	3	0.5
Zn	3	0.6
As	6	1
Br	10	2
Mo	55	10
Cd	230	44
Sb	495	94
Pb	19	4

^aLightly loaded filters. When loading is increased, detection limits may be larger, mainly because of interference between lines in the X-ray spectrum.

^b15-min sampling at a flowrate of 0.35 liter/min.

stainless steel for about 2 hr. Sampling intervals of 320 sec were used. Figure 4 shows the element concentration in 14 sampling intervals for some elements in the fine particle fraction. Welding was performed with coated electrodes; the starting time for each electrode is given in the figure. As marked in the figure, during part of the time, a local exhaust was used. The variation of elemental concentration during the 14 intervals covers about three orders of magnitude. This is an illustration of the potential and capability achievable when the personal sampler is used in connection with a sensitive elemental analysis system. The total irradiation time, when including the time for sample-area shift, is less than 4 min when 18 time-fractionated samples are analyzed with a fully automated system. Work on automating the analysis system and on modifying the computer program for simplified and standardized analysis of the samples from the personal sampler is in progress.

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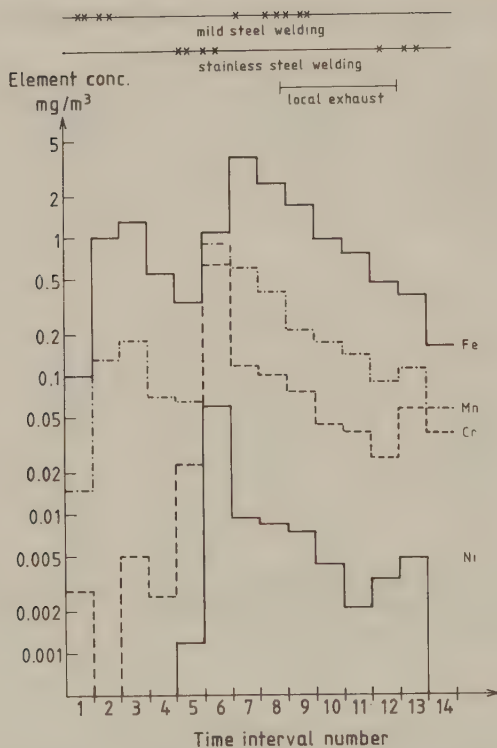


Figure 4. The result of a simple performance test of the sampler in the breathing zone of a welder. After sampling 14 intervals, each 320 sec long, the fine particle fraction samples were irradiated by protons at a current density of 200 nA/cm^2 for a 10-sec irradiation time. The results for iron, manganese, chromium and nickel are given for each interval as well as the starting time for each welding electrode and the interval during which the local exhaust was used.

ACKNOWLEDGMENT

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PERFORMANCE OF A PERSONAL LOW-WEIGHT AEROSOL SAMPLER WITH PARTICLE SIZE FRACTIONATION AND TIME RESOLUTION

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Abstract A low-weight aerosol sampler has been developed and tested. Internal losses for both sub-micron and large particles ($< 10 \mu\text{m}$) are of the order of 5%. The size fractionation patterns indicate that the sampler may be used to collect a separate respirable fraction in good agreement with the BMRC standard and a coarse fraction determined by the inlet design.

INTRODUCTION

Personal exposure to airborne particles in the work environment is normally measured with filter units which sample in the breathing zone of the worker. This technique requires manual changing of the filters with a time resolution of the order of hours. In toxicological and epidemiological research access to a large amount of detailed exposure data is highly advantageous. When identifying sources and developing suitable aerosol elimination techniques it is necessary to study the variation in the aerosol composition with high time resolution and in different particle size fractions.

To facilitate the collection of this kind of data an automatic low-weight two-stage aerosol sampler has been developed (Bohgard *et al.*, 1981). In combination with suitable analytical techniques the elemental composition of two particle size fractions can be determined with a time resolution of the order of minutes. During the last decade such a suitable analytical method, PIXE (Particle Induced X-ray Emission analysis), has been developed at our institute. A simultaneous determination of all elements heavier than phosphorus in small samples ($> \mu\text{g}$) and with low detection limits ($< 0.001 \mu\text{g}$) can be obtained within seconds to minutes (Johansson *et al.*, 1970; Akselsson and Johansson, 1979). It has been demonstrated by Bohgard *et al.* (1981) that a combination of this type of sampler and very fast PIXE analysis (10 sec per sample) allows sampling with a 15 min time resolution and detection limits well below current threshold limit values for most elements of hygienic interest.

TECHNICAL DESCRIPTION

In Fig. 236 the current version of the sampler is shown from above with the lid removed. The sampler body is machined out of plastic (PVC). A battery operated pump is connected to "OUT" drawing air at a flowrate of 0.4 l/min into the sampler through the inlet "IN". The aerosol enters the sampler through a circular impaction nozzle directed towards one of 18 collection spots along the circumference of a plastic disk (a). The larger particles impact on a thin foil (b) covering a hole in the plastic disk and supported from beneath by an aluminium wheel (c). The smaller particles proceed bending around the edge of the wheel. Another coaxial wheel carries a similar plastic disk with holes covered by a Nuclepore filter. A mouthpiece (d) sucks air through the filter and the small particles are deposited on the filter.

After completion of a preset sampling interval the coaxial impactor filtration wheels are rotated by an electric motor (e) through an angle defined by an optoelectronic sensor (f) and sampling is re-commenced on fresh impaction and filtration surfaces. To avoid significant clogging of the filter, which would decrease the flow-rate and thus alter the sampling characteristics, the pressure drop over the filter is measured by a pressure transducer. A microprocessor controls the sampling times and automatically changes sample spots when the pressure drop becomes too large. The length of the sampling interval is stored in a memory for subsequent read-out. The electronics is carried together with the pump in a belt which is fastened around the waist.

The weight of the sampler itself is under 300 g and it can be carried close to the breathing zone during work without any significant inconvenience.

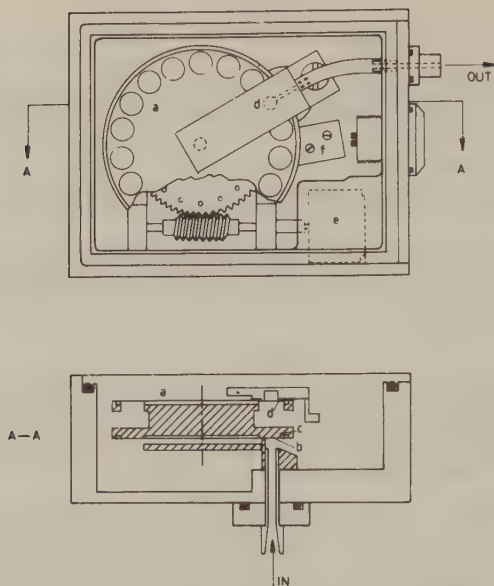


Fig. 236. The sampler seen from above and a cross section A-A from the side. The symbols (a) to (f) refer to the discussion in the text. Dimensions of sampler body (mm): $90 \times 70 \times 35$.

TESTING PROCEDURES AND RESULTS

In designing samplers intended for use in the work environment care has to be taken to meet existing standards. Normally samples are taken at a flow-rate of about 2 l/min with or without pre-collectors. For different reasons, given in detail in the paper by Bohgard *et al.* (1981), the flow-rate of this sampler is only 0.4 l/min but despite this it should sample as representatively and reproducibly as the present standard samplers. The filter stage is assumed to collect the respirable fraction according to the BMRC-standard (BMRC Panels, 1961) and consequently the impaction stage is designed to collect particles with a 50% cut-off diameter of about 5 μm .

Filter efficiency

In the paper by Bohgard *et al.* (1981) there is a detailed discussion on the choice of filter material for an earlier prototype and a description of the procedure used for filter testing. The filter selected for the current version is Nuclepore with 0.3 μm pore diameter and the pressure drop at 0.4 l/min will be about 160 torr. The minimum efficiency was measured and found to be $91.5 \pm 0.5\%$ for particles with a diameter of 0.035 μm and for a diameter of 0.1 μm the efficiency is better than 98%.

Internal losses

For sub-micron particles the sampler was tested with an aerosol of CuSO_4 produced with the equipment shown in Fig. 237a. A collision atomizer (TSI 3075) produced a polydisperse aerosol. An Electrostatic Classifier (TSI 3071) was used to select a well-defined particle size and after passing a 85 Kr source the aerosol was drawn through the sampler without any filter and into a condensation nuclei counter (TSI 3020) at a flow-rate of 0.3 l/min (nominal flow for the TSI 3020) measuring the number concentration of particles. The penetration was determined by comparing the concentration with and without the sampler and the results are shown in Fig. 238 (circles). The penetration decreases for particles below 0.05 μm due to increasing diffusion. For particles larger than 0.05 μm , however, the losses are about 5%. The added effects of high penetration through the filter and increasing losses in the sampler yield total losses of about 20% in the interval 0.03–0.05 μm but if not used for very special aerosols with extremely small mass median diameter these losses will be insignificant in mass determinations.

When measuring the penetration with a non-conducting interior the losses were $> 25\%$ for 0.2 μm particles but then the interior of the sampler was coated with a conducting layer then the losses decreased to about 5%.

The sampling efficiency for small particles including the filter stage was determined by producing monodisperse aerosols as described above but from methylene blue. The aerosol was homogenized in a mixing chamber and

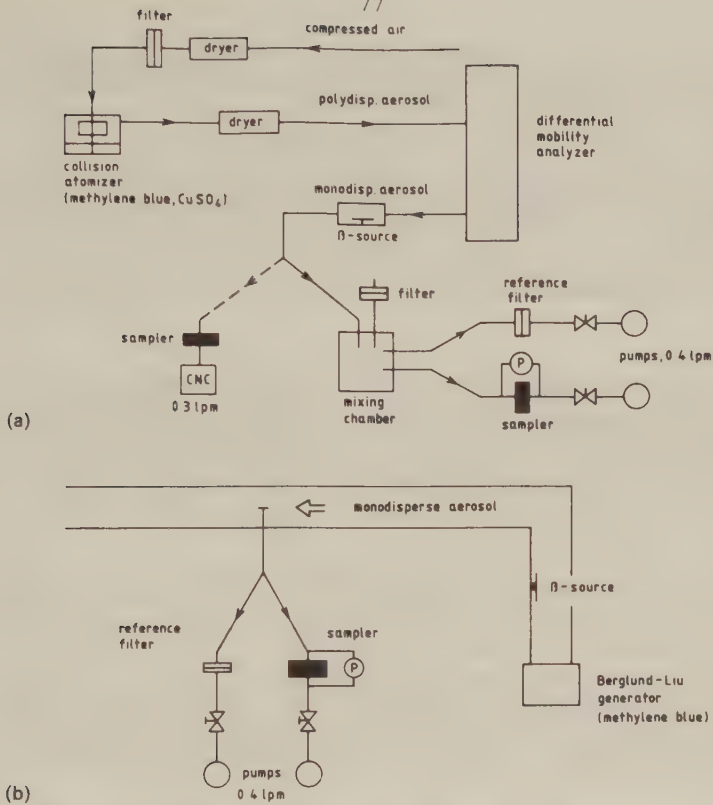


Fig. 237(a) The experimental arrangement for efficiency calibration using sub-micron particles produced in a laboratory. (b) Equipment for efficiency calibration for large particles and for testing of the particle size separation characteristics.

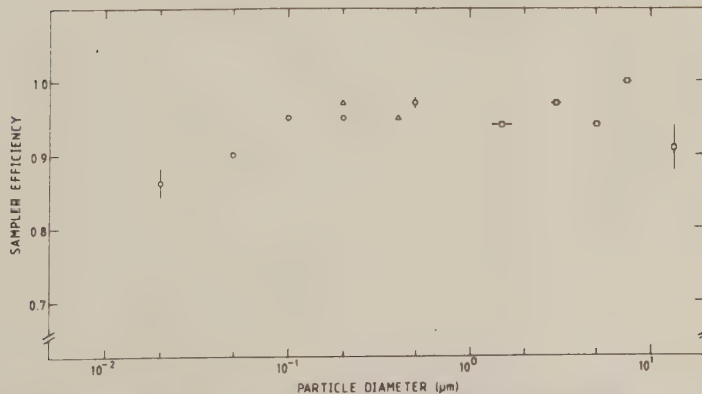


Fig. 238. Sampling efficiency vs. particle diameter. Below $1 \mu\text{m}$ the diameter is determined by an electrostatic classifier and above $1 \mu\text{m}$ the aerodynamic diameter, as determined by an optical microscope, is used. The error bars indicate one standard error on the mean for the ordinate and are estimated for different particle sizes. For sub-micron particles the symbol $\circ$ shows results from penetration measurements and Δ results from comparison with a reference filter. The symbol $\square$ shows results from efficiency determination for large particles.

sampled with the sampler and a reference filter (Nuclepore, $0.4\ \mu\text{m}$ pore diameter, $\Delta p = 10$ torr) simultaneously (see Fig. 237a). The collected particles were dissolved in ethyl alcohol and the masses determined by a spectrophotometer (Unicam SP1800, 660 nm). The results of the efficiency calculations are given in Fig. 238 (triangles) and are in good agreement with the results from the penetration measurements.

For particles larger than $1\ \mu\text{m}$ in diameter a vibrating orifice generator (TSI 3050) was used to produce monodisperse aerosols of methylene blue (see Fig. 237b). After neutralizing the aerosol with a radioactive source it was led into a small wind tunnel ($d = 0.11\ \text{m}$). A sampling probe was placed in the air-stream and aerosol was drawn into a tube eventually dividing into two equal lines, one with the sampler and one with the reference filter connected. The flow-rate in each line was $0.4\ \text{l/min}$. Equal mass was collected in each line (within 2%), for particles below $6\ \mu\text{m}$ in aerodynamic diameter. For larger particles consecutive samples were taken with constant output (within 3%) from the generator.

The mass of methylene blue collected by the reference filter was compared to the added masses on the impaction and the filtration stages in the sampler. The results are given in Fig. 238 (squares) indicating a sampling efficiency of about 95% , except for particles larger than $10\ \mu\text{m}$ for which the uncertainty in the efficiency determination is rather large.

Sampler inlet

At present the inlet of the sampler is designed to meet the Agarwal-Liu criterion for accurate sampling in calm air (Agarwal and Liu, 1980) for particles below $35\ \mu\text{m}$ aerodynamic diameter. An investigation by Fairchild *et al.* (1980) using a sampler with similar flow and inlet diameter ($0.51\ \text{m}$ and $4\ \text{mm}$ respectively) showed it to collect true concentration in calm air to within 20% for particles below $25\ \mu\text{m}$. The air velocity in most work environments is normally very low but due to turbulence and re-distribution of sedimented dust very large particles may enter the sampler possibly causing erroneous elemental results. The use of a pre-collector based on inertial separation should, however, eliminate these problems.

Particle size fractionation

A discussion on the choice of cut-off diameter and surface material for the impaction stage is given in the paper by Bohgard *et al.* (1981). The impaction substrate in these tests consisted of Nuclepore membranes coated with a thin layer of Apiezon grease. The s/w -ratio was chosen to be 1.3 (s = jet-to-plate distance and w = jet width) and the Reynolds number is about 300 . To facilitate the transport of the smaller particles to the filter stage a small fence was attached to one side of the impaction nozzle forcing the air to move in the direction of the edge of the impaction wheel.

Using the experimental arrangement shown in Fig. 237b the characteristics of the stage were determined. In Fig. 239 is shown the mass deposited on the impaction stage relative to the total mass collected in the sampler. The internal losses shown in Fig. 238 have been disregarded. The 50% cut-off diameter is $5.5 \pm 0.2\ \mu\text{m}$ which is somewhat higher than the calculated value. As can be seen in Fig. 239 a slight decrease in the nozzle diameter and the following shift in the cut-off value would most probably give separation characteristics which would fit the BMRC-curve.

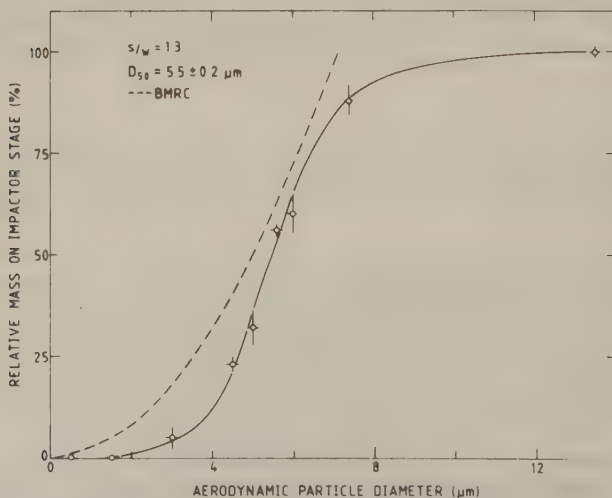


Fig. 239. The mass collected on the impaction stage relative to the total collected mass as a function of aerodynamic particle diameter. For the ordinate the error bars shown one standard error on the mean. The dotted line shows the BMRC standard for respirable sampling.

indicated by the dotted line, rather nicely. Consequently the more sophisticated multi-jet impaction stage suggested by Marple and Rubow (1981) designed to fit the BMRC-curve does not seem justified in this case.

CONCLUSIONS

An automatic two-stage low-weight (300 g) aerosol sampler for breathing zone measurements has been constructed and tested. The tests show that the sampler is capable of collecting a separate respirable fraction in good agreement with the BMRC-standard as well as a coarse fraction determined by the inlet design. The internal losses are about 5% for the particle sizes of most importance for hygienic evaluation.

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